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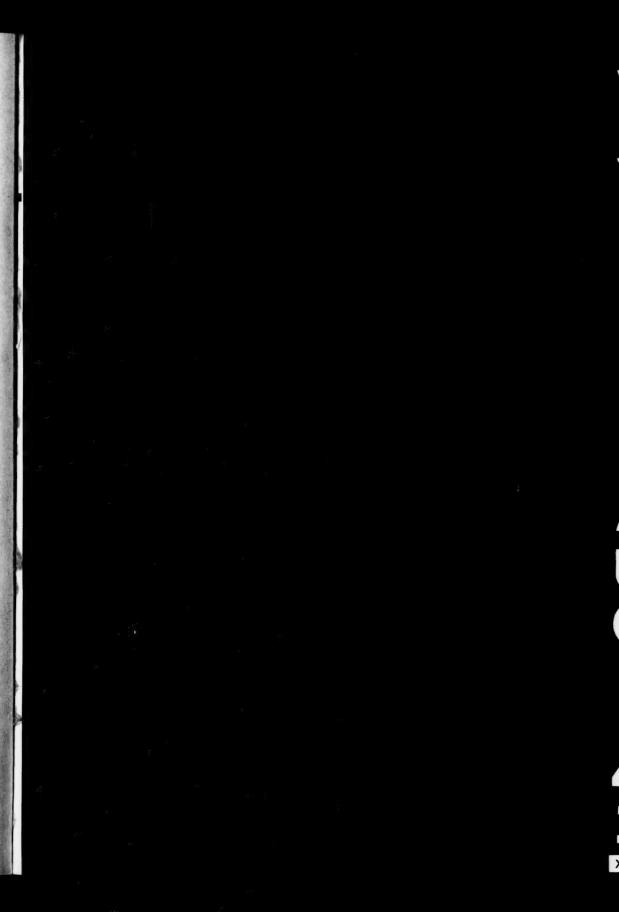
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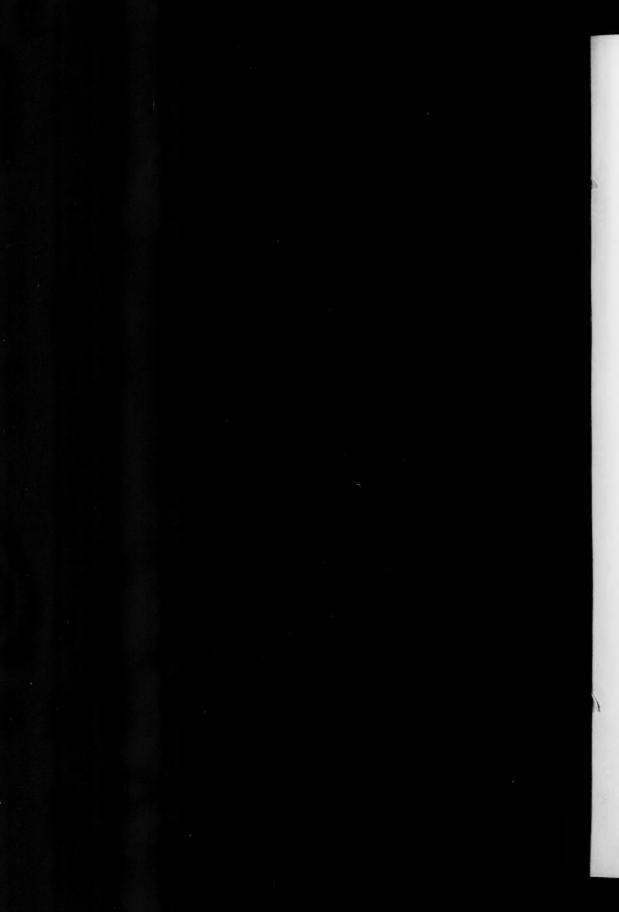
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### JOURNAL OF THE SCIENTIFIC LABORATORIES OF DENISON UNIVERSITY

The entire file of volumes 1 to 13 was destroyed by fire; no publications issued prior to 1907 are now available. Volumes 14 to date may be obtained from the editor at \$2.00 per volume, with the exception of volume 15, the price of which is \$1.00. Separate parts, as listed below, may be purchased at the prices indicated.

# The contribution of Astronomy to general culture; Edwin B. Frost. 12 pp. The geological development of Ohio; F. Carney. 15 pp. The relief features of Ohio; F. Carney. 13 pp., 1 fig. Geographic conditions in the early history of the Ohio country; F. Carney. 20 pp. **VOLUME 14** 3 figs **VOLUME 15** VOLUME 16 Articles 1-3, pp. 1-120; June, 1910. \$1.00 The metamorphism of glacial deposits; F. Carney. 14 pp., 7 figs. Preliminary notes on Cincinnatian and Lexington fossils of Ohio, Indiana, Kentucky, and Tennessee; Aug. F. Foerste. 81 pp., 5 figs., 7 plates. The abandoned shorelines of the Oberlin Quadrangle, Ohio; Frank Carney. 18 pp., 5 figs. Articles 4-7, pp. 119-232; Dec., 1910. \$0.75 Standardization of well water in the vicinity of Granville, Ohio; Lily Bell Setton. 5 pp. Chapters on the geography of Ohio; F. Carney. Transportation; 11 pp. Economic mineral products; 47 pp. Glaciation in Ohio; 48 pp. Articles 8-12, pp. 233-346; April, 1911. \$0.75 The abandoned shorelines of the Vermilion Quadrangle, Ohio; F. Carney. 12 pp., 2 figs. The Morcer limestone and its associated rooks in the VOLUME 19





#### WHAT STUDENTS WANT IN AN INSTRUCTOR

L. C. STECKLE

Received May 15, 1941; published October 28, 1941

As a project during the discussion of rating scale technique each member of a class in Business and Industrial Psychology was requested to construct a rating scale. For the manifest purpose of uniformity the students were instructed to make this a scale for a teacher of Business and Industrial Psychology. No suggestions were given concerning what particular characteristics were to be selected. Each student was to construct a scale which, from his own point of view, best would indicate the degree to which the instructor possessed those traits the student felt were requisite to teaching ability.

Since the scales were to be graded as a regular course project, some means of identification was necessary. To this end each student was assigned a number and was told to place this rather than his name on the completed report. These numbers were written on slips of paper and passed out.

A grading committee of three was elected by the students (secret ballot), and the scales when completed were given directly to this group. The committee was to examine each scale, assign a letter grade to it on the basis of thoroughness, choice of items, carefulness, insight into rating scale technique, etc. and to make a frequency count of the traits. From the frequency tally so compiled the committee made a single master scale. This scale contained only those items which the class as a whole had indicated in terms of their frequency of occurrence as being important in teaching ability.

Insofar as could be determined the students responded to this as a regularly assigned task in rating scale construction *per se*, and not as an indication of the traits they expected a teacher to possess.

The indirection here would seem desirable. It was felt that rather than ask the students to list the traits they wanted to find in instructors it would be better to have them isolate the characteristic, define it and determine its internal gradations (degree of possession by ratee), in agreement with usual rating scale methods. Such a procedure should emphasize those traits which had come through general class room observation to be considered requisite to good instruction from the students' point of view rather than the attributes of good instruction as such, involving course-products, wishful thinking, campus gossip, by-products of "bull-sessions," etc.

Three freshmen, fifteen sophomores, eleven juniors and eight seniors participated in the experiment. The committee of three¹ (two juniors and one senior) did not construct individual scales. Its function was to grade the 34 scales turned in and to construct the master scale. Continuing the game, copies of this final scale were given to the class and the instructor was rated by each student. The data from these ratings were tabulated and discussed in class.

The master scale contained nine items which by rather overwhelming majority were indicated as being important. The items and their definitions follow (the five-steps in terms of which ratings were to be made are omitted):

#### 1. Competency:

Does his presentation of the subject matter indicate sound training plus a thorough grasp of the material?

#### 2. ATTITUDE:

Is he apparently interested in having the students comprehend the subject?

#### 3. Poise:

Is he adept in handling the class room situation? Is he easily disconcerted by difficult questions or student misbehavior?

#### 4. NEATNESS:

Consider the personal appearance of the teacher in the class room and on the campus.

 $<sup>^{\</sup>rm 1}$  The writer wishes to express his appreciation to Mary Todhunter, Ray Hudson and Franklin Turnbull for a task well done.

#### 5. Courteousness:

Is he polite, civil and respectful to the students with whom he deals?

#### 6. Organization:

Does the course show evidence of fore-thought and an integration of basic material?

#### 7. SUPPLEMENTARY MATERIAL:

- (a) Is there sufficient supplementary material presented?
- (b) Is it presented in a manner beneficial to the students?

#### 8. Testing:

Are the tests as given the most conducive to bringing out and stressing the important elements of the course?

#### 9. FAIRNESS:

Does he make an obvious attempt to deal justly and impartially with his students?

In addition to the five-step scale itself, each item was followed by a "behaviorgram" consisting of instructions to list instances in support of the opinion stated. This, of course, served the function of making the ratings more objective by insisting that the rater validate his judgment in terms of actual observed behavior.

It is notable that only three items (1, 6, 7) refer to sheerly intellectual qualities. The remaining six have to do with personality traits, appearance and impression. It is difficult to state precisely what conclusion should be drawn here. Perhaps it is true as H. B. English recently stated; "The teacher must be an actor!"2—A statement of the student attitude implicit in the scale well might be "We assume that he knows his stuff; can he get it across?" In this connection it is interesting to note that an analysis of the labor turnover in 76 corporations showed that personality traits accounted for 86.4% of all failures on the job (4).

It is also interesting that the scale should bear such close resemblance to the carefully constructed Purdue Rating Scale (6) which was designed especially to measure the instructor in terms of the students' yardstick. That such scales actually measure what they are designed to measure has been attested abundantly (1), (2), (3), (5).

<sup>&</sup>lt;sup>2</sup> Address before Alpha Psi Delta; Ohio State University, 1937.

Obviously there are definite instructorial traits for which the student looks. The extent to which he finds them determines in large measure the instructor's success and, perhaps, his peace of mind.

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#### CHEMISTRY AND MODERN LAUNDRY PRACTICE

#### EARL R. HAYNES\*

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#### INTRODUCTION

In writing a paper of this type, it is always a problem to know just what material will hold the most interest for the potential reader. Even after the selection of the material has been made, the question of the manner and style of presentation offers a problem of equal weight. In the following paragraphs I shall attempt to present to you, the reader, my solutions of these problems.

\* Editor's Note.—The following quotation from *Denison University Bulletin* (Announcement by the Department of Chemistry) Vol. 40, No. 11 (September, 1940) is self-explanatory. The thesis submitted by Earl R. Haynes is printed without corrections or changes.

"WOODLAND PRIZES IN CHEMISTRY. Under the terms of the will of J. Ernest Woodland two prizes have been established in memory of his father, William Henry Woodland. These prizes are to be awarded annually as follows:

"(a) One hundred and fifty dollars to the student, in full and regular standing in any course in Denison University leading to the degree of Bachelor of Arts or Science, who shall prepare under the direction of the head of the Chemistry Department of Denison University, and present at the end of his or her junior year,

Regarding the first of these two questions, it is my opinion that an adequate answer is offered by the title of the manuscript, "Chemistry and Modern Laundry Practice." Obviously, the bulk of the material presented must be relevant to the subjects of chemistry and laundry practice. More specifically, the material should present the chemistry involved in modern laundry practice. It was with this object in mind that I began the preparation of the manuscript. As I wrote, I noticed that an element of disproportionality arose. It frequently appeared that operations which constituted an important part of the work of a laundry plant held very little of interest as far as a chemical study of the process was concerned; these operations were strictly mechanical in nature. As a consequence, it was necessary to limit the amount of space devoted to these processes; the reader will note that these topics were not omitted, but merely assigned a proportional "interest factor" as regards the chemical viewpoint. From this discussion it is obvious that the length and the degree of detail of treatment of any topic is dependent upon its importance to chemical study.

Inasmuch as this manuscript is meant to treat of the relations between chemistry and the laundry industry, and not to function as an elementary textbook of chemistry, it has been necessary to assume some knowledge of chemistry on the part of the reader. In deciding upon the "level" of discussion, I have come to the

the best original thesis on some phase of chemistry in its relation to industrial or everyday life.

<sup>&</sup>quot;(b) Fifty dollars to the student, in full and regular standing in any course in Denison University leading to the degree of Bachelor of Arts or Science, who shall prepare, under the direction of the head of the Chemistry Department of Denison University, and present at the end of his or her junior year, the second best original thesis on some phase of chemistry in its relation to industrial or everyday life.

<sup>&</sup>quot;The purpose of these prizes is to stimulate a wholesome interest in the practical applications of the science of chemistry.

<sup>&</sup>quot;For 1940-1941 the subject of the thesis is Chemistry and Modern Laundry

<sup>&</sup>quot;Students contesting for these prizes must register formally with the Department on or before November 15, 1940, and theses must be submitted in final form on or before May 15, 1941."

conclusion that the principal readers of this thesis will consist of those whose training in the sciences will have included chemistry corresponding in comprehensiveness to that which is studied in the freshman year of college under the general title of "General Chemistry." At times it may seem that the discussion has fallen to a more elementary level; this simplification, at least where done intentionally, is intended to emphasize some particular point or

points which are deemed important.

With this plan in mind, I have begun the writing of the manuscript with a discussion of one of the fundamental processes in successful laundering, water softening. Since the water which has been softened is used in some manner or other in practically all parts of the plant, it has seemed fitting that the treatment of this process should precede the other discussions. In a like manner, detergents are used in many ways in the modern laundry; therefore, the second chapter deals in a general manner with this topic and supplies a foundation for the later discussions. The later chapters present, in a "flow sheet" manner, the actual processes involved in laundering, drycleaning, and allied arts.

It has been my intention to make the discussions as general as possible in order to prevent a falling into a "rut" by the description of one particular plant. If only one plant is used as a background, it is highly probable that many interesting possibilities of discussion will be overlooked, inasmuch as no one plant utilizes all methods of laundering and drycleaning. In a like vein, burdensome insignificant details have been eliminated in so far as possible; with this in mind, I have avoided the use of a preponderance of equations and formulae, except where they are pertinent. It is hoped that this plan will save the reader a perusal of pages of data which do not add to the value of the paper.

For purpose of convenience I have placed the references for each chapter at the end of that chapter. A complete listing of the sources of material will be found at the end of the manuscript.

EARL R. HAYNES

Granville, Ohio April 26, 1941

#### PART ONE-LAUNDERING

#### CHAPTER I

#### WATER SOFTENING

Laundries, in common with most other modern industrial plants, make extensive use of water in their work; water is used not only in the integral and fundamental processes of laundering, but it is important also for its functions in the form of steam. Unfortunately, however, sources of soft water for industrial purposes are extremely rare; consequently, most laundries are equipped with some means of softening water.

It will be recalled that water may possess two types of hardness: "temporary" hardness, due to the presence of the acid carbonate ion....so-called because it may be removed by boiling, and "permanent" hardness, due to the presence of calcium and magnesium ions combined with anions other than the acid carbonate.

As has been stated above, the acid carbonate ion may be removed by boiling; as an industrial process, however, this method has little practical importance. A more practical method is the use of hydroxyl ion to neutralize the acid carbonate, forming the normal carbonate, which in the presence of, or by the addition of, calcium ion yields a filterable precipitate. The hydroxyl precipitates magnesium and iron as insoluble hydroxides. The remaining calcium salts, i.e., the calcium ion, may be removed by the addition of a salt containing an anion which will combine with the calcium ion to give an insoluble salt. The processes described above are found in the lime-soda ash process of water softening and will be treated later in greater detail.

Before describing the various processes in use in the practice of water softening, it might be well to consider the consequence of a "hard" water. The chief disadvantage to be found in the use of hard water, also common to many industries other than laundering, is in the formation of boiler scale and allied incrustations. On heating water having a considerable amount of temporary hardness, a layer of calcium carbonate may be deposited on the inside surface of the boiler and its adjacent tubes. This layer, having a low constant of thermal conductivity, (1.0 to 2.0 ×

k 10<sup>s</sup>, where k is expressed in calories/cm. sec. degree C.), lowers the efficiency of a boiler to an alarming degree. If this layer is one sixteenth of an inch thick, it may lower the efficiency of a boiler 20%, i.e., one fifth of the heat supplied to a boiler may be deflected up the chimney (1). It can be readily seen that this is a major problem to a laundry or any other plant which uses steam power. In addition to this chemical precipitation, the deposition of calcium and magnesium sulfate, caused by the evaporation of the solution when steam is generated, adds to the scale formed and is often considered to be a chief source of boiler scale.

Another problem offered by hard water results from the presence of salts of iron or manganese. Both of these, and they are frequently found together, are capable of forming oxides and hydroxides, ranging in color from light brown to black, which will stain linens and other fabrics. The well known "rust" around water sources is the result of the oxidation and/or hydroxide formation from the iron and manganese salts present in the water.

Soap, which is essentially a mixture of sodium (or potassium) salts of several higher fatty acids, will react with calcium or magnesium salts in solution to form insoluble calcium and magnesium esters. These esters, since they are insoluble and cannot be used for cleaning, constitute a waste of soap. These curds of insoluble calcium or magnesium soaps may become enmeshed and incrusted in the fabrics and cause the material to be stiff and brittle after ironing; fabrics so affected experience a great loss in tensile strength. It is therefore desirable that their formation be prevented by the removal of the calcium and magnesium ions before the soap is added.

In addition to the reasons mentioned above for the softening of water, it is often stated that the salts of calcium, magnesium, iron, and manganese found in hard water may harm fabrics directly by reacting with them chemically and causing their premature disintegration. While this statement is perfectly true, practice has revealed that it is not the major problem that it appears to be. Staining and economic waste have taken the

spotlight in the list of evils accompanying the use of hard water, while this chemical disintegration has remained in the background since its effects are not so readily noticeable.

The first, and older, method of water softening is known as the "lime-soda" process. This process is based upon the addition of carbonate and hydroxyl ions to the solution. The cheapest source of these ions is a mixture of calcium hydroxide and sodium carbonate. Precipitates of calcium carbonate and magnesium hydroxide are formed; these are removed from the solution by subsequent settling and filtration. Equations for the chemical reactions involved follow:

1. Acid carbonates removed.

 $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ 

- 2. Aluminum, iron, and magnesium removed.  $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$
- 3. All calcium removed. (sulfates and other salts)  $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$

The calcium carbonate, the aluminum, iron, manganese, and magnesium hydroxides are then removed by settling and filtration.

Water which has been correctly subjected to the lime-soda process will at best contain 4 to 5 parts per million of calcium ion in the water, but more often leaves several times this amount. It is necessary in practice to add somewhat larger amounts of chemicals since the reactions are incomplete and a part of the reagents supplied may be lost through occlusion in the precipitates (2).

It will be noticed from the above equations that the sodium ion added to the water is never removed. The sodium salts formed increase the tendency of the solution to foam during boiling, since foaming is a phenomenon of solutions, not of pure liquids. In the more severe cases of foaming water may be thrown out of the boiler with subsequent damage to the piping and machinery involved. Control and suppression of foaming consists mainly in intelligent regulation of the amount of dissolved solids in the water of the boiler.

The alkalinity should be kept down to the minimum necessary to give protection against corosion, and the concentration of salts should be lowered at intervals by removing a part of the boiler water and replacing with feed water. There are conditions under which some foaming is inevitable, if other troubles are prevented, but very efficient mechanical separators are available that will prevent water passing from the boiler with the steam (3).

Another of the disadvantages attending the use of the lime-soda process is the fact that the hardness of the water must be determined at regular intervals by an analyst in order that the lime-soda mixture will not be added in excess; the effects of an excess of sodium carbonate have been treated immediately above, and the effects of an excess of lime, forming calcium carbonate, are only too obvious.

Sodium aluminate is often added to aid coagulation of the precipitates and to effect a more rapid settling. It may be remarked here that some supplies of water contain mud and other suspended matter which is removed by this settling and filtration process, which may or may not be abetted by the use of some compound of aluminum to form the gelatinous aluminum hydroxides.

Lime-soda softeners are of two general types, intermittent and continuous. The intermittent softener consists of one or more large tanks or reservoirs arranged for the introduction of the necessary chemicals, for the introduction and subsequent decantation of water, and for the removal of the precipitate by means of sludge valves. These intermittent softeners are limited in their scope, and are not in general usage.

In the continuous type softeners the water is not static, but is kept moving at a speed which allows the reactions to go nearly to completion. By means of baffles and directed flow, the sludge is separated from the softened water; some little remaining precipitate is subsequently filtered out, often expedited by the use of sodium aluminate or other aluminum compound.

The methods described above may be carried on at the temperature of the water supply, and accordingly are called "cold process" softeners. An unduly large amount of calcium and magnesium is left in the water by the cold process softening, and

such water is likely to produce some sludge and scale in boilers and the associated pipes.

The so-called "hot process" softener is essentially the same in construction as the continuous cold process softener, except that exhaust steam is introduced with the feed water and the reagents. As a consequence, the temperature of the mixture is very near to that of boiling water. The result is that the reactions are very rapid and go nearly to completion. The solids settle rapidly to the bottom and the decanted water is given a minimum of filtration and passed directly to the boiler or receiving equipment.

Often the lime-soda process is combined with a phosphate treatment; the lime-soda is added in the cold-intermittent process, and the phosphate is then added in a manner very similar to that described above for the hot process lime-soda treatment. The net result of this composite treatment is the lowering of hardness to practically zero and the increasing the pH to 10 and above (4).

Although the description of the lime-soda process has been quite lengthy, its importance is not of the magnitude that one might infer. During the last few years a new, more convenient method of water softening has been introduced under the tradename of *Permutite Process*, but is often called the "zeolite process."

This method is based upon the use of an artificial or natural zeolite mineral, approximately of the formula Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·6H<sub>2</sub>O. If this zeolite is placed in contact with water containing calcium or magnesium ions, the zeolite is transformed; the alkali metal (usually Na) is released as an ion and is replaced in the insoluble compound by the calcium or magnesium ions. If all the compound except the sodium is designated as Z, the reactions are:

$$\begin{array}{l} Na_{2}Z + Ca \rightleftarrows 2 \ Na + \underline{CaZ} \\ Na_{2}Z + Mg \rightleftarrows 2 \ Na + \underline{MgZ} \end{array}$$

Hence the calcium and the magnesium are removed from the solution and sodium enters the solution. The transformation is generally considered to be selective adsorption followed by chemical reaction.

It will be noticed that the reactions are reversible. Accordingly, regeneration of the zeolite is accomplished by adding sodium ions to the solution; this excess of sodium ions drives the reaction

to the left, reforming sodium zeolite which is then ready to soften a further quantity of water. The cheapest source of sodium ion is commercial sodium chloride. The ensuing reaction is:

$$CaZ + 2 NaCl \rightleftharpoons CaCl_2 + Na_2Z$$
  
 $MgZ + 2 NaCl \rightleftharpoons MgCl_2 + Na_2Z$ 

The brine, which now contains calcium and magnesium ions, is drawn off, and, after being washed and flushed, the zeolite bed is ready for more action as a water softener. The brine as commonly used is a 10% solution and is used in such quantity that the zeolite bed can be regenerated in fifteen minutes.

The construction of the zeolite filters is quite simple and is usually planned, especially where only one plant is served, so as to constitute a compact self-contained unit. The softener consists of two perforated or porous beds, placed in a horizontal position. The upper bed contains gravel, marble or some similar substance which acts as does the ordinary sand filter, eliminating suspended materials and carbon dioxide; the lower bed is composed of a layer of zeolite superimposed upon a layer of gravel. The whole unit is equipped with supply pipes, valves, and pumps in order that the flow of liquid may be forced in either direction through the two beds. During the softening process, the flow of raw water is directed downward, i.e., through the gravel (or marble) bed first. When the zeolite is to be regenerated, the flow is usually reversed so that a flushing action may be effected. Both pressure and gravity-type installations are used; some of the larger capacity softeners are operated automatically, i.e., the periods of softening and regeneration are regulated by timing and metering devices.

The calcium content varies during a single run, ranging from 0.5 p.p.m. during the early stage to above 2.0 p.p.m. in the later stages. It will be noticed from the reactions given that no acid ions are removed and that a large amount of sodium ion is added with the accompanying increased tendency toward foaming. Often the bicarbonate content is lowered by the addition of an acid which reacts with the bicarbonates, forming carbon dioxide and water. This acid treatment is then followed by the removal of the carbon dioxide, usually by filtration with marble (5).

A combination of the lime-soda and the zeolite treatment is frequently used. Alone, the lime-soda process leaves calcium to the extent of 7–8 p.p.m., while the zeolite method permits calcium to the amount of 2–4 p.p.m. If the two processes are used in conjunction the calcium content of the water so treated is for all practical purposes reduced to approximately zero.

The addition of sodium hexametaphosphate, (NaPO<sub>3</sub>)<sub>6</sub>, or tetrasodium pyrophosphate, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, will prevent the deposition of insoluble calcium or magnesium soaps. These reagents form complex ions which inhibit precipitation of calcium salts and are usually added sometime during the washing process. Their use and appropriate concentration will be considered later in the section on the washing technique.

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- Deming, "General Chemistry," 4th ed., John Wiley & Sons, New York City, 1935, pp. 644.
- (2) Read, "Industrial Chemistry," 2nd ed., John Wiley & Sons, New York City, 1938, pp. 128.
- (3) Ibid., pp. 133.
- (4) Ibid., pp. 128-130.
- (5) Ibid., pp. 130-131.

#### CHAPTER II

#### DETERGENTS

Many substances possessing detergent properties (Latin detergeo. "to wipe away") have been used through the centuries for various types of cleansing and laundering. There are several references in the Bible in which the term "sope" is used: the following citation is found in the old testament:

"For though thou wash thee with nitre and take much sope, yet thine iniquity is marked before me."

Jeremiah 2-22.

The term "sope" probably refers to the carbonates derived from wood ashes (1). In the writings of Pliny the Elder (first century A.D.) there is mention of a crude soap made from goat's tallow and beechwood ash. Assuming that the goat's tallow was chiefly composed of stearin, and the beechwood ash to be sodium carbonate, we may conclude that a fairly satisfactory sodium stearate soap was the result (2).

While it is not the purpose of this paper to describe the manufacture of soap, but rather its use, it is none the less appropriate to observe the principles of chemistry involved in its preparation. By definition, soaps are mixtures of the metallic salts of the higher fatty acids; the fatty acids involved are most frequently palmitic, stearic, and oleic acids. The simplest method of preparing the sodium salts of these acids is to neutralize the acid with a strong base. However, in view of the relatively high price of acids of this nature, a less direct and more economical method is used. Various fats, which are the glyceryl esters of these acids, are allowed to react with a caustic alkali. The equation is:

 $(RCOO)_3C_3H_5 + 3 NaOH \rightarrow 3 RCOONa + C_3H_5 (OH)_3$ 

N.B. Potassium hydroxide may be used instead of sodium hydroxide, but it produces a "soft" soap, R—COO—K.

In practice, the strained oils and tallow are admitted to the reaction kettle along with a dilute solution of caustic alkali (12%) solution); steam is run in through the bottom of the kettle to promote the reaction. When the reaction is apparently complete, salt is added to the mixture, and the soap, which is less soluble in salt solution than in water or the other solutions of the mixture, precipitates in a solid curd at the top of the kettle. The byproduct, glycerol, is drawn off at the bottom of the kettle in the remaining liquid mixture, concentrated by evaporation, and is finally recovered by evaporation in a vacuum. The soap is then washed with brine, mixed with various supplementary materials, e.g., soda ash, sodium silicate, borax, starch, abrasives, etc., in large mixing vessels known as "crutchers," and finally allowed to stand for several days to harden. In the final step, the soap is mechanically treated to give it the desired physical form suited to the purpose for which it is to be used (3).

A number of compounds, such as sodium hydroxide, borax, and the sodium salts of weak acids, are used in conjunction with soap and are known as "builders." These substances, aside from being cheaper than soap, when used in combination with soap increase effectiveness of the soap so that the mixture excels by far the ordinary soap solution. In addition, several of these compounds, borax, for example, act as mild bleaching agents. The

important builders used today are soda ash, modified sodas, borax, disodium and trisodium phosphate, sodium metaphosphate, and various sodium silicates. Although some of the newer builders are more efficient, the sodas are still the most widely used. The action of these builders will be taken up later in conjunction with the washing process, but the prominent effects are deflocculation of dirt, neutralization of free acid, emulsification of oils, and the prevention of excessive hydrolysis of the soap. Sodium hydroxide alone is too strong to be used advantageously in this role, and sodium silicate, which has the same ability to maintain a constant pH, is used instead; it prevents redisposition of dirt on the fabrics, and protects the metal walls of the vessels from corrosion in the strongly alkaline solutions (4).

Laundry soaps correspond roughly to the "commercial" grade of chemicals in respect to their purity. They may contain free alkali in reasonable amounts unless they are especially designed for use with woolen and silk garments (5).

A principal constituent of most laundry soaps is rosin. The most active constituent of rosin is abietic acid. Rosin, abietic acid to be exact, saponifies according to the following equations:

$$C_{19}H_{29}COOH + NaOH \rightarrow C_{19}H_{29}COONa + H_{2}O$$

This rosin soap is saponified either directly with the soap in the same kettle or separately in its own kettle, to be mixed in later in the crutcher. When the percentage of rosin used exceeds 30%, the resulting soap is soft and sticky. This soft soap may be slightly hardened by the addition of sodium silicate. The so-called "special" grade of laundry soap contains not more than 15%, the ordinary grade may contain as much as 25%. Soap which contains rosin produces lather quicker and easier than the pure soaps; nevertheless, although the soaps which are free from rosin and fillers are slower in dissolving, they are probably better where soft water is used than are the rosin soaps (6).

Naphtha, derived from the distillation of petroleum, is an ingredient in some laundry soaps because of its solvent action on grease. If it is present in sufficient quantity to act as a solvent,

its presence in laundry soaps is extremely valuable. Its use alone as a solvent will be treated later in the chapter on dry cleaning.

It is readily concluded that the cheaper grades of soaps, having free alkali, rosin, and other fillers, may be used only on coarser materials (white sheets, blankets, towels, etc.) which are not easily damaged. For the daintier fabrics, and for woolens and silks, the higher grade neutral laundry soaps must be used to prevent damage to the cloth. Animal fibers, such as wool and silk, are easily damaged or disintegrated upon treatment with even dilute solutions of alkalies, especially at high temperatures. Regardless of the material, the daintier fabrics lose color and are otherwise weakened if washed with alkaline soaps. Even though complete immediate disintegration may not take place, these fabrics have a strong tendency to rot and shrink when continually treated with alkaline soaps. To overcome this difficulty, soaps are produced which have no fillers of any type, and which are entirely free from alkali. These neutral soaps are usually free from any great amount of moisture, and are manufactured in thin flakes which produce abundant lather with a minimum of mechanical agitation (7).

Within the last ten years several new detergents have been developed for home and laundry use. For the most part these are sulfates or sulfonates. One type of these detergents is the sulfuric acid esters (sodium) of higher alcohols with ten or more carbons. They may be used in hard water or salt water, or in slightly acid solutions, where other common soaps would not function. The type formula for these soaps is RCH<sub>2</sub>OSO<sub>3</sub>Na, and an example is CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OSO<sub>3</sub>Na, sodium lauryl sulfate. Well known trade names of such products are *Gardinal*, *Orvus*, and *Dreft*. Another type of very similar properties is found in the Igepons; these differ from the above types principally in the possession of several double bonds in the molecule (8).

These detergents of the alkyl hydrogen sulfate variety are not as efficient as soaps and in addition are more expensive. Their chief virtue for the commercial laundry lies in their comparative freedom from alkali and other fillers. As a consequence they are used in place of neutral soaps in the washing of dainty and special fabrics, and in the shampooing of rugs.

For their various types of washing processes laundries usually

buy two principal types of soaps, the cheap rosin-filled soaps, and the more expensive high grade soaps, which are more nearly neutral. The minimum requirements of these two types of soaps, manufactured from a standard high grade of fats and oils, are stated in the limiting specifications of the U. S. Bureau of Standards as follows:

Special Grade Laundry Soap

Not to contain more than:

- 1. 0.2% sodium hydroxide
- 2. 1.0% sodium carbonate
- 3. 1.0% total, chloride plus sulfate
- 4. 0.1% insoluble matter
- 5. 15.0% rosin

Ordinary Grade Laundry Soap

- 1. 0.5% sodium hydroxide
- 2. 2-6% sodium carbonate
- 3. 2.0% total, chloride plus sulfate
- 4. 1.0% insoluble matter
- 5. 25.0% rosin

More than 20% water in either grade is considered excessive (9). For different types of washings, the proper soap is compounded with various builders and materials according to formulae which have been previously approved by the American Laundrymen's Association of Joliet, Illinois. In this manner each type of fabric is washed separately from other fabrics in a soap solution which is suited to its demands. The separation and treatment of the various types of fabrics will be treated later under the washing process. It is sufficient to note here that the soap mixtures for the different washes are compounded in the laundry from the two fundamental grades of soap, both of which are mixtures in varying proportions of the sodium salts of palmitic, stearic, and oleic acids.

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#### CHAPTER III

#### ACTION OF DETERGENTS

Of all the work of a laundry, the most important of its functions is that of washing, for it is in this process that the textiles are actually cleaned, and that is the reason for which they were sent to the laundry in the first place. In the preceding chapter we have observed the nature of the detergents used, and, since the chemistry of the actual washing process will be treated in a later section, it is the purpose of this chapter to study the cleansing action of soap, the most important of detergents.

There are several more or less mechanical actions in the operation of cleansing, and, since these involve little or no chemistry, we shall dispense with them rather perfunctorily. First among these mechanical actions is that of solution. Certain parts of the matter which constitutes the soil of the cloth are soluble in soap solution (water); these soluble substances are dissolved, aided by the agitation of the wash solution, and are carried off as the solution is drained and discarded. There are other particles, usually quite large, which are detached mechanically from the fibers of the cloth by the action of the suds; particles of this nature are usually little more than in contact with the surface of the textile and can usually be observed when the garment is shaken vigorously; they are commonly spoken of as dust.

The study of the cleansing action of soap belongs primarily in the realm of physical chemistry and has to do with surface tension and colloids. A soap solution is actually a colloidal dispersion, with the soap as the disperse phase and the solvent as the dispersion medium. It is with the properties of this colloidal dispersion that we are here concerned. The principal theory concerning the washing action of soap, which, incidentally, is now generally accepted, assumes that the dirt which is to be removed is held to the surface of the garment by an enveloping grease film. This grease or oil film is practically insoluble in water, and must be removed before the dirt particles will be loosened. Soap is the agent which breaks up and removes this hydrocarbon film (1).

In the discussion on the composition of soap we observed that its molecule contained a long hydrocarbon chain combined with an atom of sodium. When soap is dissolved to form a solution. the sodium atom is found to be more soluble in an aqueous medium than the hydrocarbon chain. Hence, at the surface of the soap solution the molecules tend to regiment themselves in such a way that all the "sodium ends" of the molecule are lowermost and are submersed in the aqueous medium; this leaves the hydrocarbon chains as the sole components of the surface of the liquid, thus giving the solution the corresponding low surface tension of a hydrocarbon. When the soap solution comes into contact with an oil surface, the hydrocarbon chains form a suitable solvent and the oil film is adsorbed to it, with the consequent formation of the minute droplets which constitute an emulsion. This phenomenon is known as preferential solubility (2). The soap, in addition to being an emulsifying agent, acts also as a protective colloid so that the oil droplets remain permanently as the disperse phase of the emulsion.

A second effect of this low surface tension of a soap solution is an alteration of the surface condition of the cloth fiber and the adhering substance resulting in a weakening of the force of adhesion. Actually the colloidal particles of the soap solution are adsorbed by the dirt particles, but the dirt particles are carried off by virtue of the excess of soap solution (3). The particles which previously clung firmly to the fabric are made to transfer themselves to the surface films surrounding the air bubbles that make up the foam or suds, and are washed out along with the suds in the rinse (4).

The colloidal solution of soap possesses some power as a peptizing agent for the smaller hydrophobic dirt particles. In the presence of a soap solution some of the particles readily form an emulsion which is removed by thorough washing out with water (5).

Occasionally soap has some cleansing power because of the alkaline reaction of its hydrolysis products. In such cases the alkali formed, sodium hydroxide, reacts with substances of a fatty or acidic nature and expedites their removal by the soap solution. This was one of the earlier theories concerning the nature of the cleansing process, and, although it does constitute a small part of the cleansing process, it is not the quality to which may be ascribed the primary detergent action of soap.

Thus we see that soap, aside from being merely a liquid and a solvent, cleanses by means of preferential solubility, by virtue of its low surface tension, emulsifying and peptizing powers, and through its alkaline reaction in aqueous solution. It is by a combination of all these properties, with a predominence of a few, that soap gives such an astonishing performance in the washing process.

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#### CHAPTER IV

Washing Process—Retrospect, Load Preparation, Sudsing, pH Control, Bleach

The chemical history of laundering is quite interesting for us to look back upon, for it presents us with a development of the practical side of chemistry with which we are here concerned. The early laundress (we assume femininity) recognized the solvent power of water; she washed her clothes in the running brook

and the water dissolved out the dirt. The process of solution was hastened by the use of a mechanical agitation in the form of beating or rubbing. This method was dishearteningly slow, so she cast about for some cleansing agent which would speed up her labor without (apparent) damage to her clothes. As has been noted in Chapter II, the use of a crude soap extends back into Biblical times; it appears, however, that this knowledge was wasted upon a large part of the world's populace, for the use of even a crude soap was exceedingly infrequent during the medieval period.

Its place was taken by a highly accessible material, urine, the alkaline nature of which had been learned in some remote age. Public collections of urine furnished the populace with a sufficient supply of cleansing agent gratis. During a later period, wood ashes were taken from the housewife's fire, covered with water, and the potash was dissolved or "leached." This potash and/or lye aided measurably to the cleansing process, but was unduly destructive to clothing. To overcome this grease or tallow was added to deaden the action of the caustic, thus making a kind of crude soap. This type of soap-making has persisted into the present century, and it is only in the last decade that the mass production of inexpensive household soap has discouraged the housewife in the use of a homemade soap (1).

In modern laundry practice, branch offices or trucks are the immediate means of obtaining the "family wash." The garments and fixtures are then taken to the laundry proper and are immediately marked or designated in some manner with the owner's name and address. This may be done with small metal tags or markers of other composition, with a "fast" ink on the hidden part of the material, or by segregation with net bags, in which the fabrics remain until they reach the finishing stages of the laundering process. An additional precaution is the counting before and after the laundering and finishing, a practice which protects the customer against the unnoticed loss of any of his articles.

After the demarcation according to owner, the articles are then classified by experts into various categories relative to types of material, color, delicacy, etc. The classification is based pri-

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marily upon the kind of fabric and its color, since there are many different groups of clothing which may not be washed together; certain materials and colors are influenced by the chemicals used and the temperature of the wash water. Silks and rayons, cottons and linens, and woolens are separated. These categories are then subdivided into whites, fast colors (light), and fugitive colors (dark). This classification yields nine main divisions. In addition, there are articles of mixed fabrics or colors, which are usually included in one of the above groupings. There are also a number of special types of materials, such as rugs, curtains, blankets, sweaters, furniture covers, awnings, pillows, and quilts, which must be treated separately, frequently in very small washing machines or by hand. Usually one more division of articles, in which there is no chemistry involved, is instituted for the convenience of the laundry; this classification groups all socks together, all shirts together, all handkerchiefs together, etc. This subdivision allows similar articles to follow the same paths through the laundry, and hence allows them to receive appropriate treatment (2).

Regardless of the category in which the material is placed, it receives a laundering which is practically identical in principle for all types concerned; variations occur in the soap formulae, the temperature, the length of washing, and in other small details. These variations, however, are based upon the chemical and mechanical treatment which each type of fabric will stand, and, while they involve some chemical study, they rightly belong in the realm of textile chemistry and are beyond the scope of this

paper.

The marked clothes, or the clothes in the net bags, are placed in the washing machines. These washing machines are long metal or wooden cylinders about 4 or 5 feet in diameter and about twice or three times as long. One cylinder is within the other, and each has sliding doors to permit the washing to be placed and removed; the inner cylinder revolves back and forth, a few turns each way. The outer cylinder is equipped with inlet and outlet valves to admit and discharge washing and rinsing water. For illustration, see Fig. 1.

Clean, softened water is first admitted to the loaded machine, followed by steam to raise the temperature to between 100 and 160 degrees Fahrenheit, depending upon the type of material to be washed. The operator in charge then admits a proper amount of a mixture of soap solution and builder. This first sudsing is run for about ten minutes, drained, and a second suds is admitted with an increase of about ten degrees in temperature. This

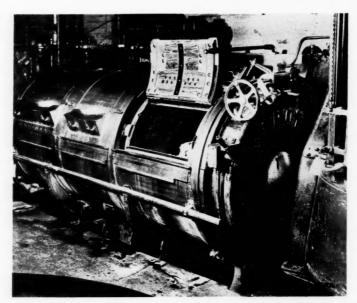


Fig. 1.—Laundry washer; located at the Licking Laundry, Newark, Ohio. Photo by author.

procedure is repeated until from four to six sudsings have been run. The maximum temperature reached ranges from 100 to 160 degrees F., and is determined by the type of material being washed.

The sudsing mixture consists of neutral (approx.) soap and builder. It is readily concluded by the reader that the higher class laundries use the nearly neutral oleic type soaps with the concurrent greater expense and higher quality work. The soap



and the builders are mixed in varying proportions according to the type of fabric being washed.

The builders used give an alkaline reaction in water and have a slight detersive action. Their alkalinity serves to neutralize the free acids, i.e., sweat and other body acids. In addition the builders serve other important needs such as the emulsification of oils, the deflocculation of dirt, and the prevention of excessive hydrolysis of the soap. As has been mentioned in the chapter on soaps, the mixture of soap and builder is much more efficient than either one used alone. Among the substances used as builders are soda ash, modified sodas, borax, disodium and trisodium phosphate, sodium metaphosphate, and various sodium silicates. Although some of the newer builders are more effective. the sodas are still among the most widely used of the builders. Sodium hydroxide is rarely used, since it is prone to be too vigorous in acting; sodium silicate acts in the same constructive manner as does sodium hydroxide in that it will preserve the same constant pH until it is used up; it prevents redeposition of dirt on the fabrics and protects the metal walls of the washing machines from the corrosion encountered in strongly alkaline solutions (3). Too great an excess of sodium silicate, however, hinders to a marked extent the detergent action of soap, and hence should be avoided (4).

Control of the pH of the washing solution is of greatest importance. Although the smaller laundries frequently do not have any apparent means of pH control, it is actually controlled by the proportions of the washing mixture. The pH of the sudsing mixtures ranges from 9 to 11, and is dependent upon the type of material being washed; animal fibers, i.e., silk and wool, are easily damaged by continued contact with solutions of high temperature or strongly alkaline solutions (above pH 8 or 9), while vegetable fibers, e.g., cotton and linen, have a much greater resistance to the action of alkali and heat.

The actual means of control of the pH consists of a device for determining the pH of the solution, and a means of changing it. In the smaller laundries a color comparator set, employing phenol red, or some such appropriate indicator, is used; the colors obtained with the indicator and a sample of the solution in question

are matched with a set of standards. Adjustment is effected by admitting to the washing solution more alkali or some weak acid. The large laundries use a more accurate type of pH determination. Frequently they employ a device such as the *Leeds and Northrup* "Micromax," which may be used not only to record pH, but also to control it automatically.

As white fabrics approach the last sudsing they carry with them a yellowish tinge which is the result of the prolonged treatment with alkali soap. In order to restore the whiteness, in so far as possible the original whiteness, a bleach is added at this stage. The basis of practically all laundry bleaches is sodium hypochlorite, NaClO. When this substance dissociates in water, a strong oxidizing agent (bleaching agent), hypochlorous acid, HClO, is formed, and the organic coloring matter present is oxidized to colorless materials. The bleach as purchased by the laundry is known by the commercial name "HTH" (High-Test Hypochlorite) and is mixed with soda ash and water to yield the

bleaching solution (5).

The primary function of a bleach is to whiten cotton and linen fabrics; a function of secondary importance is the removal of residual stains which have resisted the action of soap and alkali. A bleach's ability to perform these functions is rated by "bleaching activity." Tensile strength losses increase, however, with an increase in bleaching activity. Bleach can, therefore, be an aid to good laundering only to the degree to which bleaching activity is controlled within useful limits. When it is used in excess of 2 quarts of 1% solution per 100 pounds of dry weight in the load, bleach becomes detrimental to the tensile strength of fabrics. This bleaching activity is largely influenced by the amount of available chlorine in the bleaching solution. A secondary influence is that of the pH and the temperature; bleaching activity increases with an increase in temperature and a decrease in pH (6). In ordinary practice the pH is maintained at this point between 10.0 and 11.0. Within the range of temperature and pH commonly employed in the washroom, it has been found that variations in temperature have a greater influence upon bleaching activity than do variations in pH (7). It is readily concluded, therefore, that proper control of temperature and strength of the

bleaching solution is of the greatest importance when maximum bleaching activity with a minimum loss of tensile strength is the desired end.

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#### CHAPTER V

## Washing Process, cont'd.—Rinsing, Souring, Bluing, Finishing

From what has preceded, it will be noted that the washing solution at the bleaching stage has a pH of about 10–11 and a temperature of 150–160 degrees F. Immediately following the bleaching are from four to six rinses with successively higher temperatures. The chart at the end of this chapter shows the temperature, pH, running times, etc. of a standard washing process, as presented by the Laundryowners Association of Joliet, Illinois, and will serve to show the reader the different conditions which are imposed upon fabrics under consideration.

The next step in the washing process is that of "souring," socalled because of the acids used. Souring is essentially a corrective process, and exerts important influence upon the color of the finished garments. As has been noted above, the solution as it reaches the rinsing stage is markedly alkaline; we have observed before that most fabrics, especially animal fibers, are harmed by the presence of alkaline solutions. Therefore, to avoid leaving the fabric in contact with deleterious chemicals, the alkali is neutralized with some type of weak acid or acid salt; if strong acids were used, oleic, palmitic, and stearic acid would precipitate.

The most common sours, with comments on each, are listed below (1):

- 1. Acetic acid—satisfactory sour, but may leave objectionable odor.
- 2. Formic acid—highly satisfactory sour, no odor, but harmful to skin of operator.
- 3. Oxalic acid—good sour; useful in removing rust stains.
- Sodium silicofluoride—fairly insoluble and must be used in powder form; specific for removal of iron stains (not necessarily rust.)
- 5. Sodium acid fluoride—effective in removal of iron stains.
- Ammonium salts of 4 and 5—greater solubility and may be used as solution.

It is readily concluded that the above salts hydrolyze in solution to form highly active acids, fluorosilicic and hydrofluoric.

On first inspection it might seem that in order to neutralize the residual alkali it would be necessary to merely add the sour until a pH of 7 was reached. However, it must be remembered that some sodium carbonate is present, and, since its "neutralization" takes place in two steps, only half of it is neutralized at pH 7. The products of its neutralization would be carbonic acid and a salt (nearly neutral), thus yielding a solution of pH less than 7. Experimentation shows that its complete neutralization is effected at about pH 5.0. The 50% mark is reached at pH 8.0. The relative souring power per pound of various sours shown in the following table, designating acetic acid as unity (2):

Acetic acid 56%	1.0
Acetic acid 99.5%	1.77
Oxalic acid	1.70
Sodium acid fluoride	1.72
Ammonium acid fluoride	1.88
Formic acid 90%	2.10
Sodium silicofluoride	2.28
Ammonium silicofluoride	

It has been shown by experiment that, regardless of the sour used, souring to pH 5.0 represents 95 to 100 per cent neutralization of the alkalinity, and, in the case of acetic acid, this figure would represent an excess of 25% of sour.

Another element in determining the amount of sour used is known as the absorption factor; this is the result of the fact that a large amount of alkali remains in solution in the fibers of the fabrics and yields a higher alkalinity than is found in the water which is merely in contact with the fabric. The pH considered in the above discussions was that of the water in contact, and not absorbed in, the fabric. It is this absorption of alkali that prevents an efficient rinsing and makes souring necessary. No set rule is given for the compensation of this variable, but the common practice is to adjust the sour until the water which is thrown from the fabric by the centrifugal extractors has a pH of 5.0 (3).

Sours perform an important function with regard to stains arising from various compounds of iron. These stains are caused by corrosion in the pipe lines, by the presence of iron in the local water supply, providing it has not been removed, or by contact of the clothes with iron containers. These stains are collectively referred to as rust stains, although many other types of iron compounds may be present. By reference to the chart listing the various sours at the head of this chapter, it will be noted that these stains are best removed by oxalic acid or the acid fluorides. Routine souring will not remove these stains, even though the appropriate reagents are removed; we have observed that souring to pH 5 is adequate for the neutralization of the alkalinity, but in order to remove iron stains in addition to this neutralization, it is necessary to use a large excess of sour. When a strongly acid solution of this type is used, it is necessary to rinse the load afterward until a pH of 5 is again reached (4).

Occasionally white cotton and linen pieces which have been repeatedly laundered and soured will develop subsequent yellowish stains when laundered without a sour. It appears that, when fluoride sours are used, complex salts of iron are formed; these, although they are not completely soluble, are colorless and hence are not noticed on the garment. During the subsequent launderings with the sour absent, the complex iron salts are converted into the oxides and hydroxides of iron and have the consequent staining power. These stains must then be removed by the use of iron-removing fluoride sours or with oxalic acid solution (5).

A question which may occur to the reader is that concerning the harmful effects of sours upon clothes. Experiments show us that the so-called "tendering" effect, or loss of tensile strength, occurs only when the pH of the wash solution is less than three. The following table gives the pH of solutions (sours) which have equivalent neutralizing values (6):

Name of Sour														pH (0.08M)
Acetic acid 56%	 							 						3.5
Oxalic acid														
Sodium Bifluoride	 							 						3.4
Ammonium Bifluoride	 	 						 			 			3.4
Formic acid 90%	 							 			 		 	3.4
Sodium silicofluoride														3.6

<sup>\*</sup> Below 3; has tenderizing effect.

From the above table we observe that pH is an indication of the tendering effect of a sour, but is not an indication of the neutralizing power. Souring to a pH of less than 5 is uneconomical and involves risks to the articles being washed (7).

In determining the pH of the sour bath the same method is used as was described in Chapter IV. The colorimetric equipment differs only in that different indicators are necessary. The indicator best adapted for control of the sour bath is methyl red, whose range is pH 4.4 to pH 6.0. However, stable color standards for comparison are not always available, and hence bromcresol green, range pH 3.8 to pH 5.4, is often substituted.

The sour is often a prerequisite for good bluing. Although there are "blues" which will function in a neutral or alkaline solution, for the most part the more efficient blues work in only an acid bath. The blues which are in common usage today are three in number; they are ultramarine blue, Prussian blue, and aniline blue. Of these three the last is the most important from the standpoint of modern laundry practice. Aniline blue comes either as an acid aniline dye (non-sour blue), or as an alkaline aniline dye (sour blue). The sour blue works more evenly and is more reliable in practice than the non-sour blue, and hence enjoys a larger spread of practice than does the non-sour blue. There are from 3000 to 5000 different types of aniline dyes, and the formulae of most are trade secrets. If insufficient sour is used with a sour-blue, the alkali may decompose the dye or it may cause streaks in the fabrics. The bluing bath is run immediately after the sour and is conducted in warm (not above 120 degrees F.) solution (8).

Souring is normally conducted at suds water level at a temperature of 120 to 125 degrees F. After a five minute run at this temperature, cold water is added, just prior to bluing, so that the load may be "pulled" (removed) without discomfort. Some laundries prefer a so-called "hot sour," conducted at a temperature of 140 to 145 degrees F. This practice is necessary only when local conditions, relative to water supply, render the cooler sour ineffective. In the performance of a souring operation it is necessary to remember that, if sufficient sour is being used to remove stains, the pH will be below 5 and it is then imperative to rinse the load until pH 5 is reached; it will be noted that the load should always have a pH of 5 before souring is discontinued (9).

As the load is removed from the washer, it is placed in a cylindrical perforated metal "cage." This cage is placed in a machine, in the manner of a cylinder standing on end, and is rotated at a speed of from three to five thousand revolutions per minute. Thus a large part of the water in the fabrics is removed in this "extractor" by the use of centrifugal force. "Damp wash" is taken directly from the extractor and is delivered to the customer; the remaining wash is taken to the finishing rooms of the plant.

Some of the garments are to be starched; this starch "paste" is made by adding powdered starch to water, in the proportion of about 10 ounces to the gallon, and is "cooked." Starch, of the empirical formula  $(C_6H_{10}O_5)_n$ , is composed of small granules which have thick envelopes; these envelopes are ruptured by cooking, and thus allow the inner more soluble colloidal substance to form

The "thin boiling" starches, now so extensively a dispersion. used, are manufactured by acid hydrolysis. These "thin boiling" starches penetrate fabrics very readily and quickly set to a gel upon cooling. Recently the manufacturers have developed a non-congealing thin boiling starch which remains a liquid even in the cold state. Variation of the mixing process produces many different types of starch, each suited to some special type of work; hence the actual preparation of a starch paste in an individual proposition, peculiar to each laundry and to each requirement in that laundry. Each source of starch yields a material of different properties, e.g., corn starch is hard and brittle, while wheat starch is tough and pliable; accordingly, blending is practiced to give a finished product of the desired characteristics. Aside from improving the initial appearance of the laundered garment, starch tends to "keep it clean" longer; this property is dependent upon the fact that the "glazed" fibers of the material take up dirt particles far less readily than the unprotected fibers (10).

After the appropriate articles have been starched, the load is taken to the ironers. Flatwork is ironed on large steam heated rollers which are covered and connected by endless revolving belts. Wearing apparel is finished on smaller pieces of apparatus known as presses. These are similar and sometimes identical to the types of presses used by your tailor to press your suit; usually, however, they are especially designed machines, each adapted to one particular type of garment. Quite often these garments are touched up by hand after they leave the production line, at which time they are inspected for needed mending, buttons, etc. After finishing is completed, another inspection is made, and, if the garments pass this, they are sorted and wrapped for delivery to the customer.

Housewives have long debated the advisability of sending their wash to the laundry, where it will be washed in the same wash water that is used for the washing of garments belonging to many other families. The danger of acquiring an infectious disease by this means seems quite imminent. Nothing, however, could be farther from the truth; almost every compound which is used

in the laundering is germicidal in its effect. That soap possesses strong bactericidal properties is attested to by the fact that surgeons "scrub up" with soap for ten minutes before an operation. The high temperature of the water used in washing is fatal to practically all germs; surgical instruments are sterilized by this method. Hypochlorites (the bleach) are widely used by physicians for disinfection, and form the active constituent of the famed "Dakin's solution" which was used so widely during World War I. All of the sours used in laundry practice today are

Conduct of a standard laundering (12)

BATH	TEMP.	TIME	pН	MATERIALS
1st suds	100 deg. F.	10 min.	11.1	Soap & builder
2nd suds	120	10	11.1	Soap & builder
3rd suds	140	10	11.1	Soap & builder
4th suds	150	10	11.1	Soap & builder
5th suds	155	10	11.1	Soap & builder
6th suds	160	10	11.1	Bleach, soap, builder
1st rinse	175	3	_	
2nd rinse	185	3	-	
3rd rinse	185	3	_	
4th rinse	185	3	_	
5th rinse	140	3	-	
Sour	130	5	5.0	Sour
Blue	110	5	5.0	Blue

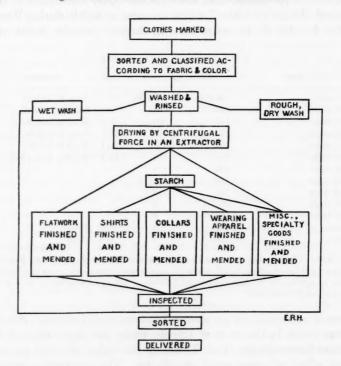
N.B. The running times listed above do not include changing and handling time. pH listed is based upon optimum results with a particular soap and builder, but is applicable to most soaps and builders. Temperatures based on a white cotton and linen load.

strong antiseptics, as are most substances of acid nature. Studies were made in the state of Illinois, under the supervision of the State Bacteriologist, T. J. Testin, to determine the total germicidal effect of commercial laundering. The conclusions reached were as follows: the washing process destroys a minimum of 99.96% of all bacteria present, and the routine ironing and pressing brings this figure up to 100%. Similar studies made on home laundering showed that the washing there destroyed only 25 to 50% of the bacteria, and that the ironing could not be relied upon to eliminate the remaining 50% (11). The propriety of

patronage of a commercial laundry, reputable, of course, can hardly be questioned in view of these data.

It is the author's hope that through the medium of this paper a survey of the principles of chemistry involved in modern laundry practice will have been briefly presented. A survey of this type

Fig. 2.—FLOW CHART—LAUNDRY PROCESSES



must necessarily be concerned with the introduction of each of the many phases of chemical processes involved, rather than a complete exposition of these processes. Upon each of these topics many books have been written; each of these topics is reducible to still more subdivisions. Accordingly, it has been the aim of the first part of this paper to expose the reader to the essential unit chemical divisions of modern commercial laundering, without an irrelevant dissection of these unit parts to the first principles of chemistry; a reduction of this sort can be found in any text of elementary chemistry which has the teaching of chemistry as its purpose, and which assumes a null knowledge of chemistry on the part of the reader.

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#### PART TWO-DRYCLEANING

#### CHAPTER VI

# DRYCLEANING PROCESS

Twenty years ago drycleaning consisted of immersing garments in a tub of gasoline, agitating them with a paddle, hanging them up to dry, and pressing them. If all soil and stains had been removed, all well and good; if soil and stains remained, they were accepted with a shrug of the shoulders and had to be countenanced with determined resignation. Today we see this struggling, haphazardous infant "drycleaning" grown into strong healthy manhood. With less resignation and more determination the

modern drycleaner attacks his problems; it is primarily for this reason that the drycleaning industry does a volume of business amounting to more than \$500,000,000 annually. The craft has now come to deserve a share of our attention equal to that held by laundering (1).

Drycleaning has as its purpose, in common with laundering, the removal of soil, spots, and stains of divers sorts from garments and other fabrics. The distinction between laundering and drycleaning lies in the type of solvent and detergent used. The solvent is an organic liquid which is colorless and looks like water, but, unlike water, it does not cause skrinkage, wrinkles, loss of press, loss of dyestuff in garments which have been correctly processed in manufacture, and it will remove many substances (soil) which are not affected by laundering. Like the laundry industry, drycleaning makes use of soaps, especially prepared for use with the organic solvents. For our purpose, the description of the processes is conveniently divided into four categories; drycleaning, spotting, wetcleaning, and specialties. In this chapter we shall observe the general methods of drycleaning.

As a garment reaches the cleaning plant, it undergoes a marking and classification which is practically identical with that which we have observed in the section on laundering. It is carefully marked to insure the customer against loss; notation is made of the peculiarities of the garment, rips, tears, unusual stains, special fabrics which would not withstand the usual drycleaning treatment, or any unusual construction of the garment. Wool garments are separated from the silk, linens, and other materials. Each of these divisions is further classified into white, light, and dark colors; fabrics which require special handling, such as organdie, chiffon, marquisette, and other sheer materials, are separated from the rest of the garments. The tensile strength and the finish of delicate fabrics is always given the benefit of the doubt and safe handling is the primary concern. After they have been marked and classified, the garments are sent to the drycleaning department.

At this point in some plants, the garments are given a "prespotting" treatment. The purpose of this process is to avoid

fixation of the stains and soil by the drycleaning, and to reduce the amount of difficult water spotting afterwards. Often it is necessary to use prespotters after drycleaning with a subsequent "re-run" through the drycleaning (2). These processes will be treated at greater length in the chapter on spotting.

The next stage of drycleaning is the operation of the "washer," a machine identical with, and a little smaller than, the one described in the chapter on the washing process. The solvents used in this washer may be divided into two principal types; first, the petro-

leum solvents, and second, the synthetic solvents.

The petroleum solvents, as the name implies, are derived from the fractional distillation of crude oil. Four fractions, or "cuts," are usually taken. The first cut, with the distillate ranging from 80 to 69 degrees Baume, is the light naphtha fraction; the second, ranging from 69 to 58 degrees Baume, is the heavy naphtha distillate, and it is from this that the majority of the petroleum drycleaning solvents is derived; the third cut, Baume 58 to 43, consists of high test burning oils and is likewise the source of solvents for drycleaning; the fourth cut, Baume 43 to 21, contains low test burning oils. The residue remaining in the still is principally tar. Drycleaning solvents are frequently made up of mixtures of the heavy naphtha distillate and high test burning oils (3). These naphthas are then treated with sulfuric acid; the unsaturated hydrocarbons, the potential source of objectionable odors, gummy, and resinous materials are taken up by the sulfuric acid layer and are subsequently removed. Sodium hydroxide is then added to the naphtha to neutralize any residual sulfuric acid and to remove traces of phenols, cresols, and other similar materials. Sulfur compounds which are present in naphtha often create unpleasant odors and undesirable colors in the drycleaning solvent. These sulfur compounds are removed with sodium plumbite, Na<sub>2</sub>PbO<sub>2</sub>; the plumbite takes up the sulfur compounds, separates into a layer, and the overlying layer of naphtha is decanted. Since this treatment tends to prevent and remove unpleasant odor, it is known as the "Doctor Treatment." The chemically treated nephtha is then washed with water to remove the inorganic salts remaining, decanted, and is finally

filtered through a decolorizing medium, e.g., Fuller's earth or activated charcoal (4).

A drycleaning solvent, in order to be practical, must possess a number of exacting qualities. It must not only clean well, but every trace of it must be easily removed; it must not change the shape of a garment (shrinking), and it must produce no chemical or physical changes in the garment being treated. Aside from these consumer interests, it must meet certain requirements peculiar to the demands of the drycleaning industry. Its initial cost must be low, yet the product must be stable; loss through evaporation must be at a minimum; corrosion of storage systems or other equipment must be null; it must not combine chemically with reagents used in cleaning, thus making purification and clarifying difficult; inflammability must be low; its toxic effect upon those handling it must be at a minimum.

In order that these requirements might be definite and more easily conformed to, in May, 1935, W. J. Stoddard, of Atlanta, Georgia, announced to the industry a new petroleum solvent, which has since been named the "Stoddard Solvent" in his honor. This solvent has certain standard specifications, formulated by the National Association of Dyers and Cleaners in conjunction with the Bureau of Standards, Department of Commerce. Any refinery can make a solvent which conforms to these standards and market it under their own trade name, and this practice is followed quite generally. The standard specifications for this solvent are summarized below (5):

- "1. Appearance. Shall be clear and free from suspended matter and undissolved water
- 2. Color. Shall be water-white or not darker than 21 by the Saybolt chromometer.
  - 3. Odor. Shall be sweet. (i.e., not unpleasant)
- 4. Flash point. Shall not be lower than 100 degrees F. when tested in the 'Tag' closed tester."
- "5. Corrosion test. A clean copper strip shall show not more than extremely slight discoloration when submerged in the solvent for three hours at 212 degrees F.
  - 6. Distillation range. Not less than 60% shall be recovered in

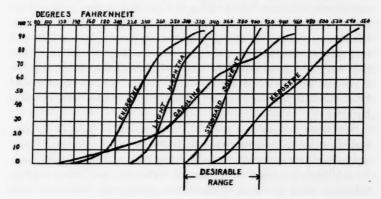
the receiver when the thermometer reads 350 degrees F. The end point shall be not higher than 410 degrees F. No tolerance shall be allowed above 410 degrees F.

7. Acidity. The residue remaining in the flask after the distillation is completed shall not show an acid reaction.

8. 'Doctor' test. Shall be negative.

9. Sulfuric acid absorption test. Not more than 5% of the solvent shall be absorbed by concentrated 'c.p.' sulphuric acid (sp. g., 1.835) (approx. 93.2%)."

Fig. 3.—COMPARISON OF DISTILLATION RANGES (6)



INCREASING WEIGHT (SPECIFIC GRAVITY)

The first three requirements, regarding general appearance, color, and odor, along with the corrosion, acidity, Doctor, and absorption tests, tend to prevent unpleasant and/or damaging aftereffects to garments undergoing drycleaning. The flash point is the determining factor of the fire hazard. Stoddard solvent, for example, will not have even a "momentary flash" at any temperature under 100 degrees F., and, since drycleaning rooms rarely reach this temperature, little attendant fire hazard is experienced in using this solvent.

The distillation range requirement possesses some little interest for a student of chemistry. Herewith (Fig. 3) will be found a

graph showing the distillation curves of various naphthas. It will be noticed that the curve of the light naphtha fraction starts to boil below 300 degrees F. Solvents of this type present a problem, not only because of the attendant fire hazard, but also because of the great loss through evaporation; the greater proportion of low-boiling constituents in a solvent, the greater the fire hazard and evaporation loss. If a solvent has an end point which is higher than 410 degrees, it will be difficult to remove the last traces through evaporation; fabrics must be returned to the customer not only well cleaned, but odorless. To evaporate completely solvents which have a high end point, it would be necessary to raise the temperature of the drying cabinet so high that many stains may be "set" and other damage to the material may ensue. According to the chart above (Fig. 3), the Stoddard Solvent's first drop would be distilled over at about 300 degrees F., which is sufficiently high for safety, and the end point would be about 410 degrees F., thus allowing convenient deodorization by heat (7).

Synthetic solvents, as used in the drycleaning industry today, are chlorinated hydrocarbons and are three in number. They are carbon tetrachloride, tetrachlorethylene, and trichlorethylene. In addition, mixtures of carbon tetrachloride and other organic solvents, such as ethylene dichloride, propylene dichloride, and benzol are often used. The properties which have interest for us are listed below (8):

DATA	CARB. TET.	TRICHLOR.	TETRACHLOR.
В.Р.	76.7 C.	86.7 C.	120.8 C.
End Point	77.0	87.5	122.0
Vap. Pressure (30 C., mm Hg).	140.0	91.0	28.0
Flammability	none	none	none

It will be noticed that none of these three is flammable. In practice, aside from protecting the lives of the employees, this property tends to lower materially the insurance rate. The low vapor pressures, especially that of tetrachlorethylene, reduce the cost of maintainance considerably through minimum loss by evaporation. The extremely short distillation ranges, about 250 degrees F. maximum for the highest of the three, allows complete

removal of the odor at a reasonably low temperature (about 160 degrees lower than for the Stoddard Solvent). In addition, the low boiling points allow easy purification through distillation.

There are several disadvantages, however, which mar the records of these three, and of chlorinated hydrocarbons in general. Some of the conditions of use tend to bring about a decomposition, forming compounds of acidic reaction which have a detrimental effect upon the metal equipment. This decomposition is brought about through three fundamental causes; first, through oxidation (air); second, through hydrolysis (water); and third, through pyrolysis (high temperatures). The first type of decomposition is accelerated by high temperatures. Hydrolysis is catalyzed by metals, e.g., iron, and by light. Oxidation may be inhibited by the use of "stabilizers," or substances which oxidize more readily than the hydrocarbon. No stabilizers, however, are known for use against hydrolysis and pyrolysis. Of the three, carbon tetrachloride undergoes decomposition most readily, and for this and other reasons is not widely used as a drycleaning solvent. The fumes from all three are toxic to humans; this property constitutes a serious health hazard (9). If trichlorethylene is used at temperatures above 80 degrees F., it has a tendency to remove some of the dye from cellulose acetate fabrics. The distribution and usage of synthetic drycleaning solvents is about 20% of the total amount of all types of solvents used. Synthetic solvents require less bulky machinery, will not burn or explode, and are somewhat easier to use than the petroleum solvents. Petroleum solvents, on the other hand, are less likely to corrode the machinery and other equipment. It still remains a matter of individual choice for the drycleaner whether to use the naphtha or synthetic solvents.

Regardless of the type of solvent, the operations fundamental to drycleaning are fairly well standardized. Since the solvent is relatively expensive, it is not discarded, as water is in laundering, but steps are taken to remove the soil and coloring matter in it so that it may be used again. There are three main types of purifying and clarifying processes; distillation, filtration, and chemical treatment.

The usual means of renewing a solvent consists of a combination

of filtration and distillation. The filter is a set of baffle plates or leaves, on which lies the cloth or paper filter. Since the surface of the cloth or paper is relatively small compared to the volume of solvent being filtered, some sort of "filter aid" is used. This filter aid is composed of a porous compound or mixture, such as Fuller's earth, diatomaceous earth, or magnesia, which cakes upon the filter and presents an immense surface to the liquid being filtered. Practice varies somewhat with individual plants, but the usual procedure is to add a small amount of filter aid to each "batch" of solvent. This filter aid, being insoluble, readily adsorbs the soil and coloring matter of dirty solvent, and settles out. After the run, the solvent plus the filter aid is pumped through the filter; the filter aid cakes on the cloth or paper screen, with it the soil and coloring matter, and the clarified solvent passes through the filter and is ready to perform again.

It will be noted that this filter aid removes only those materials which are not in true solution, such as suspended coloring matter and soil. Grease, oil, fatty acids, and other organic materials which are soluble in the drycleaning solvent, remain in solution and pass through the filter. When the concentration of these materials becomes high enough to affect the working of the solvent, the solvent is distilled. Water is removed by a trap, the oils, fatty acids, etc. remain in the retort, and purified solvent is taken from the receiving tank to be used again. In order to prevent "cracking" and to save fuel, the pressure within the system is usually reduced to about one pound per square inch; this permits the solvent to be distilled at a much lower temperature than would be possible at ordinary working pressure. With the Stoddard solvent, the distilling temperature is lowered from an average of 370 to 230 degrees F. (10).

Chemical clarification is accomplished by the use of caustic soda. A solution of caustic soda is added to the solvent and agitated. The sodium hydroxide reacts with the oils to form water soluble materials, and separates into a layer containing these aqueous solutions and settles to the bottom, allowing the floating layer of solvent to be drawn off (11).

The principal method of clarification and purification of the

present day is a combination of filtration and distillation, with the frequency and inter-relation between the two being determined by the individual drycleaner. Other methods have been proposed from time to time, for example, centrifuging, settling by gravity, and other mechanical means, but most of them require the maintainance of an unusually large stock of solvent or they have some other disadvantage which renders their use impractical.

The first run in the washer, the load being the garments, solvent, and filter aid, is called the "break," and removes the loose and readily soluble material from the fabrics. After this has been run for several minutes, the solution is drawn off, sent to the filter, and is replaced with fresh solvent. To this fresh solvent is added more filter aid and some benzine soap.

The average water soluble soap is completely saponified, contains no excess fatty acid, and is not soluble in drycleaning solvent. Since the use of solvent alone does not give the desired cleansing results, some sort of aid must be used to expedite the cleaning. The answer to this problem is the so-called benzine soaps. It has been found that, in the manufacture of soap, if a smaller quantity of alkali is used than is customary, some of the fatty acid will remain unsaponified and will be thoroughly mixed with the finished soap. This superfatted soap is soluble in, or at least miscible with, the drycleaning solvent, and a suspension results. Some soaps have been produced which go into true solution or form an emulsion with the solvent, but these are in no manner superior and need not be considered separately. The benzine soap in common usage contains from 5 to 35% free fatty acid (12).

Since the solvent used in drycleaning does not "wet" the fabrics, it is obvious that the benzine soaps have a somewhat different role to play. Since the solvent is a pure or substituted hydrocarbon, the addition of a soap does not appreciably lower its surface tension; the initial penetrating powers of the solvent are sufficient without a lowered surface tension. Benzine soaps have a lubrication action on the soil, and after it is once free of the fabric, the soap particles are absorbed by the dirt particles. By having such a small affinity for the fabric, the soap particles and

the soil are easily flushed out; because of this property benzine soaps are given the name "collectives" (13). Since benzine soaps are not alkaline in reaction, they have no effect on dyes. Their solvent action is exceedingly small and unnecessary, considering the amount of useful solvent present. Superfatted soaps tend to form an emulsion of water in the solvent, a condition exactly opposite from that found in laundering; this moisture is taken from the fabric where it would inhibit the action of the solvent. Magnesium benzine soaps tend to dissipate the static electricity formed in the washer, a factor to which has been ascribed the cause of explosions in drycleaning plants, and which, in addition, causes lint to stick to fabrics and ruin the appearance of the garment. The fact that benzine soaps form a suspension is an attribute rather than a drawback; dirty soaps must be removed from the solvent before it can be used again; this suspension is readily removed by filtration with the porous filter aid. Frequently a small amount of moisture is incorporated in the soap in order that its affinity for the "damp" particles of dirt in the fabric will be greater (14).

After a soap run has been completed in the washer, the dirty solution is drained off, routed to the filter, and is replaced with clear solvent. Again to this rinse is added filter aid to entrap particles of soap and dirt. The rinse bath is drained off and sent its way to the filter. In some plants two washers are worked in conjunction; the solvent is drained from one, filtered, and pumped to the other. In this manner a minimum of solvent is necessary and very little storage space is needed for the solvent being filtered.

When the rinse has been drained from the washer, the clothes are transferred to the extractor. The extractor is a large centrifuge which turns up from 3000 to 5000 R.P.M. Practically all of the remaining solvent is thrown from the garments by this process; the "thrown" solvent is usually drained off and sent to the filter. The garments are then placed in a warm air tumbler, a machine which actually tumbles the clothes lightly about to dry them. The vapor escaping into the atmosphere of the tumbler may or may not be subjected to condensation to save the

solvent; this is a practice which must be determined by the particular plant.

The nearly dry garments are then inspected for stains and spots, and if necessary, are sent to the spotting department. The work of this department will be treated in a later chapter. In the final process, the apparel is pressed, mended when necessary, wrapped, and delivered to the customer.

Occasionally the drycleaner may receive a garment which is too badly soiled for cleaning by the ordinary drycleaning methods, or one which is too delicate or which has a special construction and may not be treated by the usual drycleaning methods. These garments are then sent to the wetcleaning department. Wetcleaning differs from ordinary laundering in that it is practically all hand work and cleansing agents are used which are more delicate and more specific in action than is the common soap (15).

A garment which is to be wet cleaned is laid out on a table which is built into a sink. The wetcleaner uses lukewarm or cold water and a soap appropriate to the work. In the majority of the cases, a neutral soft oleic or potassium soap is used. A builder may or may not be used, according to the fabric in question. Often the work is carried out with the aid of spotting, the practice of which will be discussed in a later chapter.

If the fabric is one which might be injured by the action of ordinary soap, even neutral soap, one of the new synthetic detergents may be used. These detergents, sulfated or sulfonated alcohols, described in chapter II, are neutral reaction and will not harm any fabric or dye which is safe in water.

Another detergent which is widely used in wetcleaning is the sulfonated oil. This detergent is the product of a reaction between an oil, such as castor oil, and sulfuric acid; usually about 25% of the total volume of sulfuric acid is used; after the mixture has been allowed to stand for 48 hours, water or a solution of sodium sulfate is added. The excess sulfuric acid dissolves in the aqueous medium, two layers form, and the water layer is removed. This washing is continued until all traces of free acid have been washed away. The product is then neutralized with ammonia or

sodium hydroxide. Since compound produced had the properties of a glyceride, and yet was acidic in nature, the addition of an alkali produces a compound which is very similar to soap, yet is much more oily than ordinary soap. By virtue of its double nature, this product is soluble in water and in organic solvents. This solubility may be merely miscibility, but the desired result is secured. Thus the wetcleaner is prepared to use an agent which will unite water and oil very efficiently and easily. Sulfonated castor oil is sold under the name of "Monopole," and, if carbon tetrachloride has been added for its solvent action, it is called "Tetrapole." If the amount of sulfuric acid used is 15%, the resulting product forms a milky suspension with water; if 25% of sulfuric acid is used, the product will form a clear "solution" with water. Both of these types find use on the wetcleaner's "table (16).

Garments to be wetcleaned, since they are treated with water, are subject to some danger of shrinkage and fading. They are carefully measured before and after being washed; the dyestuff is tested to determine whether it will withstand washing; the garments are given the most careful hand treatment. Even in view of these precautions, the majority of drycleaners find it advisable to secure the customer's permission before wetcleaning a garment, and do not completely guarantee the work (17).

In the last few years fabrics have appeared which have a "chalked" finish. The use of either drycleaning or wetcleaning will remove this chalk. To restore this luster, garments are placed in very dilute sulfuric acid solution. The excess acid is squeezed out and the garment is placed in a dilute solution of barium chloride. The barium sulfate precipitates very evenly in a finely divided state and presents a satisfactory "chalk" finish. The excess sulfuric acid is neutralized with some dilute alkali such as borax or very dilute ammonia. The soluble reagents are washed out with water (18).

It is obvious that wetcleaning is carried out with all precautions which are given to any careful laundering. The water is softened and sodium hexametaphosphate is frequently used (see Chapter I).

Many dress fabrics contain sizing or weighting materials which are removed in the process of wetcleaning, or even in drycleaning. In order to restore the garment to its original shape and drape, this sizing must be replaced. The commonest size is a mixture of corn and wheat starch, the use of which was discussed in Chapter V. Occasionally the use of a hot iron or press after starching will convert the starch into dextrin, a brownish yellow compound when found on fabrics. In a situation like this, the sizing must be removed, garment resized and finally repressed with greater care (19). Other common sizing materials are olive oil, paraffin oil, gum arabic, gum tragacanth, and gelatin. Treatment with formic or acetic acid hardens these oily compounds to a gelatinous sizing.

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#### CHAPTER VII

## SPOTTING

There are thousands of types of stains which a garment may have, and more thousands of ways of removing these stains. The majority of these spotting methods constitute individual chemical reaction; to list all of them would be too great a task for a paper many times the length of this one. For our purposes it will be competent to list the various general types of chemical reactions, together with examples of each. In this way it is the author's hope that various phases of the chemistry involved will be adequately presented without necessarily including a complete textbook for a spotter's use; specific manual operations for spotting are easily found in any spotter's handbook.

The first and best known method of removing spots is by solvent action. In the last chapter we have noted the use of solvents in the general drycleaning process; the solvents mentioned there, plus a host of others, are used extensively in spotting. Solvents may be classified into two principal groups, solvents that wet and solvents that do not wet. Wetting solvents include or are associated with water; aqueous solutions are practically always wetting agents. Among the wetting solvents, aside from water, are acetic acid, ammonia, synthetic wetting agents, such as the sulfated alcohols sulfonated oils (Monopole, Tetrapole), and the substituted amides, the lower alcohols, glycerin, Lysol, and various aqueous solutions of salts. These wetting agents, when used alone or in conjunction with lubricants and emulsifying agents, are extremely useful as solvents; stains removed by them are mostly inorganic materials (1).

The non-wetting agents are the organic solvents. The three mentioned in the last chapter, carbon tetrachloride, trichlorethylene, and tetrachlorethylene, are widely used on the spotter's table, either alone or in a mixture with soap or other solvents. Among the other dry solvents are included: acetone, amyl acetate, amyl alcohol, benzaldehyde, benzol, carbon disulfide, chloroform, ether, phenol, various oils, pyridine, and naphtha (2).

Often a mixture of the two types of solvents, together with

soap or other reagents, is expedient in its action. To this end it is necessary to use some sort of emulsifying or peptizing agent, known as a carrier, in order to make the mixture homogeneous (at least for all practical purposes). Among these coupling agents or carriers are amyl alcohol, butyl alcohol, isopropyl alcohol, oleic acid, pine oil, and the most famous and widely used, Hexalin (cyclohexanol) (3). Such mixtures are effective in that they permit both wet and dry solvents to act at the same time.

A second method of spotting is called by the drycleaner "lubrication." This may range from a true lubrication with an oil or a substance like glycerin to emulsification with an agent like soap. A common agent of lubrication is a mixture of oleic acid. carbon tetrachloride, ammonium hydroxide, water, and some carrier; this forms a true soap, with the ammonium radical as the cation. Ammonium soaps are soft and of oily consistency: the union, or admixture, of a solvent, such as the carbon tetrachloride, and water yields a double action mixture. The ammonium soap tends to emulsify the moisture present in the soil in the dry solvent. Both the soap and the excess oleic acid act to a certain extent as lubricants. Other "lubricants" are the oils, e.g., pine oil, the sulfonated oils, such as monopole and tetrapole, and the "oily" substances like glycerine. The synthetic detergents mentioned before are considered lubricants. The effect of lubrication is usually a combination of the two properties of emulsification and true lubrication in variable proportions (4).

The third category of spotting is catalysis, and is known to the drycleaner as "digestion." In this method of spotting foods, protein materials, and other complex organic matter are actually digested in somewhat the same manner as digestion takes place in the stomach. Commercially produced enzymes, available in the powder form, are made into a solution, placed upon the spot, and are allowed to act for a period of time. By their catalysis, the complex insoluble matter is made into simpler soluble compounds which are easily flushed off the fabric. In the use of these enzymes, temperature is of prime importance; above 140 degrees F. many are destroyed; below room temperature their action is

greatly retarded. Some work best in acid or alkaline solution; others require a neutral solution for best results. A bit of dilute salt solution tends to enhance their activity (5).

There are two common types of enzymes, those which digest carbohydrates, and those which digest protein materials. Usually the manufacturers will incorporate a mixture of two in order to cope with various types of stains which contain both carbohydrates and proteins. These enzymes will not harm fabrics, with the exception of woolens which have been subjected to intense bleaching previously, and their solution may be used in any situation in which water may be safely used (6).

The last principal method of spotting, and the one which holds the greatest interest for us, is that of chemical action. The possibilities of chemical action are innumerable, and some chemical action is usually incorporated in the foregoing methods. The principle involved in the removal of spots and stains by chemical means is as follows: the spot or stain is treated with some agent which reacts with it to form some new compound or compounds which are invisible and will not be noticed as a spot, or which are soluble and may be flushed out of the fabric.

The removal of dvestuffs of various sorts is one of the more frequently encountered problems of the spotter. For our purposes we may classify dyestuffs as acid dyes, basic dyes, and neutral dyes. Stains resulting from dyes are frequently caused by colored soft drinks and foods, medicinal preparations, cosmetics, inks, and other dves encountered in everyday life. The problem of the spotter is remove the dye which constitutes the stain without removing the dye which was used to color the textile. The process is successfully performed only when there is a difference in the types of the two dyes. Dye color is the result of resonance of the double bonds in the organic molecule, and, since these double bonds may be altered or destroyed by oxidation or reduction, dyestuffs may be decolorized in accordance with this method. Most dyestuffs are subject to hydrogenation, and may be removed by the use of the reducing bleach, e.g. sodium bisulfite, sodium hydrosulfite, and oxalic acid. Other dvestuffs are decolorized by the utilization of an oxidant, such as peroxide, sodium hypochlorite, sodium perborate, and potassium permanganate. Dyestuffs differ greatly in their susceptibility to oxidation and reduction. Some are affected by one of these processes and not the other, while some few are removed by either (7).

An acid dye is usually removed or at least lessened in its intensity by reaction with a base; conversely, a basic dye may be affected by the addition of an acid. This rule is generally true, but is not irrevocable. Certain dyes, such as the triphenylmethane group, are decolorized by the use of ammonia; this is not strictly a bleaching action, but is a temporary condition existing only as long as the solution is kept alkaline. If the solution is neutralized, the color will usually reappear, but will be less intense. Some dyes experience a similar effect when treated with an acid, only to reappear upon neutralization. Examples of this phenomenon are the dyes found in Mercurochrome and in certain lipsticks (8).

In attempting to remove any spot caused by a dyestuff, a neutral lubricant is the first step. The addition of an acid or basic reagent may have an effect of not only not removing the stain, but also may fix the stain more or less permanently. The reason for fixation of this sort is a decrease in the size of the dye particles of the stain, with the result of making them cling more tenaciously to the fabric. This method, often utilizing heat to reduce the size of the particles, is the one by which fabrics are dyed to a permanent fastness in their manufacture. Thus the application of acids, alkalis, and other reagents to a dye stain without first removing the excess with a neutral reagent may result in a dyeing of the fabric with the stain, since these agents may dissolve some dyestuff in a cold state to a similar extent that water would in a hot dye bath of the type used in manufacturing of dyes fabrics (9).

Rust or other iron compounds may be removed by the application of oxalic acid or dilute hydrofluoric acid (or its acid salts). The addition of any common acid to a rust stain will convert the iron into a soluble salt. An example of this, shown in equation form, follows:

# $\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2 \text{ FeCl}_3 + 3 \text{ HOH}$

Iodine is frequently found as a stain on garments. Its removal is quite simple; the addition of ammonium hydroxide to the spot forms the soluble ammonium iodide; the addition of sodium thiosulfate forms two colorless water soluble compounds, sodium iodide and sodium tetrathionate. With either method, water flushing completes the process of removal. For stubborn stains dilute hydrofluoric acid or one of its acid salts may be found effective. The reaction is one of displacement; the iodine goes into solution as the iodide ion and the fluorine is liberated as the free element and is easily removed (10).

Stains from tannin constitute one of the largest groups which confronts the spotter. Tannic acid is one of the most widely distributed organic acids in the vegetable kingdom. It is an important constituent of coffee, tea, and tobacco; it is a lesser constituent of fruit juices, soft drinks, beer, cocoa, chocolate, peaches, pears, apples, and other fruits, and of grass and walnut hulls (11).

The tannins are vegetable substances which are uncrystallizable colloidal materials with astringent properties. They coagulate gelatin solution and yield colored compounds in the presence of iron salts, forming iron tannates. They are coagulated from solution by the action of various metal ions, alkalis, alkaloids, and other organic materials of a basic nature. Although the formula for tannic acid is well known, the tannins which produce stains on textiles are not the same as tannic acid; tannic acid is soluble in water, acetone, and alcohol, but the tannins are soluble in none of these solvents (12). It will probably never be possible to remove all tannin stains completely from all fabrics, since in many cases the tannin enters into chemical union with the fabrics.

Treatment of tannin stains usually consists in digestion, to remove the sizing-tannin compound frequently formed, application of a neutral lubricant to remove the excess of tannin on the fabric, and the addition of an acid spotting agent. Since the tannins tend to be precipitated by substances of an alkaline nature, the use of an acid compound will frequently reverse the reaction and make the tannin more soluble. Tannin stains on white fabrics are often subjected to oxidation and reduction in the hope that more soluble complexes and simplexes of tannin will be formed. If a tannin stain has become "set" by heat or chemical action, its successful removal is almost impossible (13).

By this time the reader may readily conclude that, in the main, spotting consists of a specific treatment for each type of stain or spot. For the myriads of possible chemical stains there are just as many individual specific chemical reactions. In the foregoing paragraphs of this chapter we have observed a few of the more important of these, together with their general applications. To continue this method of study of the chemistry of spotting would be futile and endless. It might be wise at this point to classify for our convenience the various types of chemical reactions which are encountered in spotting practice. Regardless of the stain, however, solvent action and lubrication should be tried first since these methods involve less risk to the dyestuff and the fabric and in many cases will prove sufficient. Chemical treatment is usually the last resource.

If a stain can be shown to have a definite pH, either an acid or an alkaline reaction, the process of neutralization is utilized. It has been noted before that acid dyes are frequently decolorized or removed by the addition of a base and conversely. Stains resulting from acids (or acid salts) or alkalis are usually made more soluble or colorless by neutralization. An exception to this is the tannin group; while it is acidic in nature, it is precipitated from solution by alkaline substances. Thus the removal of tannin is expedited by the use of an acid.

Metathesis is an important action in spotting. Often insoluble colored compounds are rendered soluble or colorless if one of the groups or ions present is displaced by a different group or ion from some other compound. An example of this method is the removal of a stain resulting from silver nitrate. The

silver in the compound is sometimes oxidized to the insoluble free state by the action of air and other substances. The metallic silver may be removed by the addition of a solution of iodine. The iodine oxidized the silver and silver iodide is formed; this compound is soluble in ammonia or sodium thiosulfate. The part of the stain resulting from the undecomposed silver nitrate is treated with potassium iodide; silver iodide and potassium nitrate are formed and may be removed by ammonia or sodium thiosulfate (14). Undoubtedly the compound silver nitrate accounts for a large share of the stain, and, since this reaction (for removal) takes place more readily than the other, the stains are usually successfully removed.

Oxidation and reduction both are classed as bleaching by the spotter, but a differentiation is made between the two types. Oxidizing bleaches are the most commonly used and include the hypochlorites, hydrogen peroxide, sodium perborate, and potassium permanganate. The hypochlorites undergo hydrolysis in aqueous solution to yield a mixture of hydrolysis products which includes hypochlorous acid, HClO. This weak acid is unstable and breaks down to form HCl and free oxygen; the latter is responsible for the bleaching action (oxidation) of the mixture. Hypochlorous acid may be formed by adding free chlorine to water. The reactions are:

$$Cl_2 + HOH \rightarrow HClO + HCl$$
  
 $HClO \rightarrow HCl + \frac{1}{2} O_2$ 

When any of the so-called chlorine bleaches are used, they should be followed by a treatment to remove any free chlorine which might remain in the fibers. Agents used for this purpose are known as antichlors; sodium thiosulfate is the most widely used antichlor, but sodium bisulfite and other reducing agents may be used in this capacity. Hypochlorite bleaches are safe on vegetable fibers and on the cellulose acetate fabrics, but should not be used on animal and synthetic fibers. Lowering the pH of the bleach has the effect of accelerating the bleaching action (15).

Hydrogen peroxide is one of the most desirable bleaches for use in the spotting department. It may be used without rinsing, since the products of its decomposition are water and oxygen, both of which evaporate from the fabric and leave no harmful residue, other than the decolorized material which has been bleached. In contrast to the hypochlorite bleaches, high pH values of the solution tend to accelerate the oxidation, and, as a consequence, mild alkalis, e.g., ammonium hydroxide, are often added to the peroxide to hasten its work. Sunlight and heat also have this activating effect; of the two, sunlight is the more desirable, since heat may increase the rate of reaction to an extent which is harmful to the fabric.

Sodium perborate is quite satisfactory as a spotting bleach when left to act over a period of time. It reacts much more slowly that does hydrogen peroxide, and leaves a residue which must be thoroughly flushed from the fabric (16).

Potassium permanganate is a very effective oxidizing agent for use on the spotting board, but tends to be too drastic in its action. In addition, it is quite difficult to remove completely from the fabric after the bleaching action has subsided; this characteristic may cause subsequent damage to the fabric through the action of the residual salts. The use of potassium permanganate as a spotting bleach is largely confined to the removal of stains from white fabrics and from the white areas on printed fabrics. On the printed fabrics its color makes it possible for the spotter to determine exactly what area is being oxidized, thus preventing damage to the surrounding fabric. The permanganate is reduced first to a manganate and then to a manganous salt. There is a strong tendency for various oxides and hydroxides to form, yielding brown or black residues. To overcome this difficulty, the bleached area should be subsequently blushed with a dilute solution of hydrofluoric acid or one of its salts. The manganese residue is rendered more soluble by fluorine compounds and thus permits better rinsing. As with the other oxidizing bleaches, potassium permanganate should be treated after the bleaching process with some reducing agent to preserve the fabric against subsequent over-oxidation (17).

Reducing bleaches work in a manner directly opposite from that of the oxidizing bleaches. Oxygen is usually taken from the fabric, dyestuff, or stain with the consequent alteration of the physical and chemical properties of the material in question. It seems obvious that, if an oxidizing bleach does not remove a stain, then the reducing bleach should. In practice, the oxidizing bleach is usually added first, and, if desired results are not forthcoming, the reducing bleach is allowed to react; the presence of the oxidizing bleach enhances the action of the reducing bleach (18).

In spite of the fact that there are a great number of reducing agents which could be used as bleaches, drycleaners and laundrymen have found that the original select few give performances which are but little (if any) improved upon by the substitution of other bleaches.

Sodium bisulfite, NaHSO<sub>3</sub>, is widely used in the capacity of a reducing bleach. It hydrolyzes in aqueous solution to form sulfurous acid, H<sub>2</sub>SO<sub>3</sub>, a reducing agent which is readily oxidized to form sulfuric acid. Lowering the pH and/or raising the temperature will hasten the reducing or "stripping" action (19).

A more powerful reducing agent is sodium hydrosulfite,  $Na_2S_2O_4$ . It oxidizes in a manner similar to the bisulfite mentioned above, and hence produces a like bleaching effect. In accordance with its stronger reducing powers, it will remove stains and dyestuffs which are not affected by the bisulfite. Its activity is likewise enhanced by a higher temperature and the addition of proton to the stripping bath (20).

In using any "sulfite" bleach it is essential to remove all traces of the sulfur atom, otherwise, over a period of time, sulfuric acid would be formed in the fibers of the garment and would destroy them. To affect this condition, an oxidant, such as hydrogen peroxide, is added to the reducing agent; the sulfurous acid present is oxidized to sulfuric acid. The excess sulfuric acid is then washed out and a solution of ammonium hydroxide is added to neutralize any residual acid. A thorough rinsing completes the job (21).

Often a spotter will add, for accelerating purposes, just any acid to the hydrosulfite bleach. If the acid happens to be a strong acid, in concentrated form, free sulfur will be formed and will adhere to the fibers of the fabric. In order to remove this

sulfur, it must be oxidized or dissolved in some appropriate solvent.

Within the last few years a new type of reducing agent has been put on the market. This bleaching agent is known as a "titanium stripper" and is highly useful within its limited field. Titanium strippers have the capacity to reduce completely stains on white fabrics without any trace of "over-reduction" which would produce an area of greater whiteness than the surrounding field. If these strippers are used on garments which have been cleaned with metallic soaps, yellow staining sometimes results. This condition may be corrected by soaking the fabric in a dilute solution of hydrochloric acid, treating with ammonium hydroxide, and rinsing (22).

Oxalic acid has been used for a number of years as a bleaching agent by laundrymen and drycleaners alike. In spite of the fact that it does have some action on rust and ink stains, and does possess some reducing powers, it usually does more harm than good. It is difficult to rinse out and it crystallizes in sharp edged crystals which may damage the fibers of the cloth. Because of its specific action upon iron it is often given more credit for bleaching powers than it actually deserves.

If a garment has been wetcleaned with hard water, calcium and magnesium soaps may precipitate and form curds which resist the action of the usual spotter's reagents. When this condition arises, the garment is soaked in a dilute solution of hydrochloric acid, thus forming the soluble calcium and magnesium chlorides. The fatty acid remaining may be saponified with ammonium hydroxide, forming soluble ammonium soap which is easily flushed from the garment. This condition may be avoided, even in hard water, by using sodium hexametaphosphate (chapter I) in the wash water (23).

The spotter has to face not only the problem of removing the stain, but also the one of protecting the fibers and the dyestuff of the fabric. All textile materials are damaged by some solvents, bleaches, and miscellaneous reagents. Animal fibers are easily damaged by alkalis and strong acids. Wool will not withstand excessive bleaching action. The cellulose acetate fibers dissolve

readily in certain organic solvents, such as acetone, formic acid, etc. Vegetable fibers, e.g., cotton and linen, are discolored by strong oxidation, and they are damaged by contact with concentrated solutions of the corrosive inorganic acids, such as hydrochloric and sulfuric. As we have noted before, most dyestuffs are affected by particular reagents, i.e., acid dyes by alkalis, basic dyes by acids, etc., and may have a greater or less tendency to "bleed" or be decolorized.

In spotting each particular job, the spotter must determine the type of spot and the operations necessary to remove the spot and then eliminate those operations which would harm either the fabric or the dye. The remaining harmless methods are then utilized to remove the spot. It is obvious that the spotter must be familiar with all types of fabrics and the effect of the various reagents upon them. While in a practical sense this is impossible, a good spotter must have years of experience to base his work upon, and in this manner approaches very near to "omniscience in spotting."

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N.B. All specific references in this chapter were taken from that excellent book, "The Spotting Department," by Clyde H. Covington.

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- (2) Ibid., pp. 63 to 78.
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- (4) Ibid., pp. 85, 86.
- (5) Ibid., p. 93.
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- (15) Ibid., p. 197.
- (16) Ibid., p. 199.
- (17) Ibid., p. 200. (18) Ibid., p. 202.
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## CHAPTER VIII

# RE-DYEING

Each year thousands of dresses and other garments are sent to the laundries of the United States to be dyed to a color different from the one possessed by the garment at the time of purchase. Some of these garments are white, but about ninety per cent of them are colored, thus presenting an additional problem to the re-dyer. Dyeing is an important part of textile chemistry, and, as there are thousands of dyes on the market today, the description of these dyes and their functions would constitute a tremendous work in itself. Accordingly, in this paper we can hope to cover only the most important aspects of the chemistry of re-dying.

Garments to be re-dyed must be thoroughly clean; usually such articles are drycleaned or wetcleaned just prior to the dyeing process. White garments are then ready to be dyed. If a garment is colored, the color is usually removed, but it *may* be left in to help yield the desired color by blending.

If a garment is to be bleached or "stripped," it is put into a stripping bath composed of either an oxidizing or reducing bleach, depending upon the fabric and the dyestuff. The action of these bleaches has been treated in the previous chapter; the commonest bleaches used are sodium hypochlorite, sodium hydrosulfite, and sodium perborate. The bleach is then exhausted completely by placing the garment in mild bleaching bath of opposite action (oxidation or reduction). The bleach is followed by a distilled (or soft) water rinse to insure even swelling of the fibers, a prerequisite of uniform dye penetration; the temperature of this rinse is adjusted to suit the fabric being treated.

Chemists believe that color is a property of the molecular arrangement of a compound, as regards double bonds; in organic dyestuffs, and these are by far the most important from the point of view of the laundryman and the drycleaner, certain groups are

given credit for the production of color in a compound. These groups are collectively called chromophores; examples of the most common chromophores are the nitro group, the azo group, and the quinoid group (1). Fundamental compounds which contain these groups are designated as chromogens; the groups which lend the necessary activity to the molecule, such as the amine group, the sulfonic acid group, and the hydroxyl group, are called auxochromes. For purposes of discussion in this paper we shall divide the various dyestuffs into three principal groups, according to their dyeing properties; the direct dyes, the mordant dyes, and the developed dyes (2).

Direct dyes, as the name implies, are those which react directly with the fibers of the fabric, forming an insoluble color-lake. Some dyes are direct with respect to animal fibers, others are direct to all fibers, and still others are direct toward certain

fibers, but may be mordanted on additional fibers.

Acid dyes are salts of colored organic acids and act directly upon animal fibers in acid solution. Since animal fibers are protein in nature, they contain both organic acid and amine groups; by virtue of these two groupings, they are able to react with both acidic and basic substances. A possible explanation of the chemical process of dyeing by this method is offered by Matthews (3) as follows: the sodium salt of a color acid plus sulfuric acid yields the color acid plus sodium sulfate; the color acid then reacts with the basic groups (amine) in the animal fiber to give the color-lake. In practice, Glauber's salt (sodium sulfate deca-hydrate) is added To prevent too rapid absorption of the dyestuff by the fibers; when used in this manner, Glauber's salt, or some similar agent, is known as a levelling agent (4).

The basic dyes owe a great number of their properties to the presence of amine groups in their molecules; these dyes are direct dyes for animal fibers. According to the accepted theory, the amine groups react with the acid groups of the protein molecules in the animal fibers to give insoluble color-lakes. Although basic dyes will unite readily with animal fibers in neutral solution, the rate of absorption is so rapid that uneven dyeing usually results. To prevent this condition, a weak acid, such as acetic acid, is often

added to retard the rate of dyeing; as in the case of the acid dyes, levelling agents are usually used in the dyeing bath. Basic dyestuffs, although usually more brilliant, produce colors of inferior fastness as compared to those produced by acid dyes. In view of this fact, their use is restricted to materials in which bright colors, rather than fast colors, are desired. In order to use basic dyes on vegetable fibers, it is necessary to use a mordant of an acidic nature. Tannic acid is usually used for this purpose, since it can combine with the vegetable fibers and still retain its acid properties for reaction with the basic dyestuff. It is frequently necessary to add another salt which will combine with the tannic acid to form an insoluble tannate in the fibers of the textile (5).

A third type of direct dyes are the substantive colors. These will combine directly with either animal or vegetable fibers, but, since the acid and basic dyes are more satisfactory for use on animal fibers, the substantive colors are rarely used for this purpose. An important exception to this practice is in the dyeing of a mixture of animal and vegetable fibers. The dyeing action of the substantive dyes appears to be physical rather than chemical in nature, and accordingly does not merit our attention in this discussion (6). Similar in action are the so-called "sulfur colors." These colors contain sulfur in their molecules and are accelerated by the addition of the sulfide of a strong base, such as sodium sulfide. The particular chemistry of their action is not well understood; they are widely used in the dyeing of cotton.

Mordant colors are dyestuffs which do not combine readily with the fibers, but which can be made to combine with a mordant which has been previously deposited upon the fibers. There are a number of important mordants, but for the most part they are salts of iron, tin, copper, aluminum, or various complexes of tannin. It is interesting to note that the same dyestuff will yield different colors when used with divers mordants. For example, logwood when used with an iron-tannin mordant gives blues and blacks, with tin-salts, purple, with copper, greenish black, and with aluminum, violet. These different colors produced with the same dyestuff, but with different mordants, have varying degrees of fastness; the colors obtained with aluminum and tin are extremely "fugitive" (7).

Developed colors are those which are produced in the fiber by successive contact with two or more chemical compounds which react to give the desired color. These developed colors are extremely important in the manufacture of textiles, but are rarely used in laundry and drycleaning practice. Therefore we leave these dyes with just this small mention.

We have used the term "fast" in the foregoing discussion without regard to any particular set of conditions. In a strict technical sense, however, it is necessary to specify the working and exposure conditions whenever the terms fast or fastness are used. Some dyestuffs are fast to the action of sunlight and air, but will not withstand laundering, and conversely. Whenever a garment is to be dyed, the dyer must take into consideration the use to which the garment is to be put. Evening gowns may be dyed with colors that would stand only a few hours of daylight; sport suits must have dyestuffs which are fast to sunlight, air, sweat, and other outdoor conditions. Thus it is not only the condition and fabric of the garment which determine whether it can be dyed successfully, but also its future intended use (8).

Plants, animals, and minerals of nature furnished an important source of dyestuffs until the middle of the nineteenth century. After the English chemist, W. H. Perkin, discovered mauve in 1856, interest in the production of synthetic dyestuffs rose to a new high. Through the agency of intense studies of coal-tar and its derivatives, the number of synthetic dyestuffs reached the figure of six hundred at the turn of the century and is now in excess of one thousand (9).

After a garment has been dyed, the material usually will appear to have lost body and luster. This lack of "character" in the dyed cloth may be attributed to the removal of the sizing during dyeing operations. This desizing is not an incidental by-product of the dyeing process, but is a necessary prerequisite of even penetration of the dyestuff. Occasionally the dyeing operation is not sufficient to remove the size which is present in the material and an extra operation to remove completely all sizing must be instituted immediately prior to the dyeing operation. Often this desizing may be done with a moderately warm or hot acid or alkaline solution; other situations demand treatment with a digesting agent (Chapter VII) to remove the organic sizing. As a direct consequence, the size must be replaced after the dyeing process is complete if the fabric is to regain its original luster and weight. These sizes, mentioned previously in chapter VI, are usually a gelatinous material such as starch, gum, arabic, and gelatin. Replacement sizing, however, is rarely as satisfactory as the original sizing inasmuch as the penetrability of the fibers of the cloth has been affected by the repeated chemical and mechanical treatment necessary in redyeing.

In order that the reader may gain some familiarity with the dyes used in redyeing, a brief list of the different types of dyes is presented below (10).

Acid Dyes

Naphthol Yellow S Wool Red Eosin

Benzyl Green Acid Peacock Blue

Substantive Dyes Congo Red Hessian Purple Congo Violet

Direct Fast Brown

Developed Dyes Diazo Brilliant Black Diazo Dark Blue

Diazo Brown Primuline

Basic Dyes Methyl Violet

Malachite Green Methylene Blue Magenta

Bismarck Brown Mauve

Mordant Dyes Logwood Haematin

Turkey Red

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- (4) Ibid., p. 253.
- (5) Ibid., p. 255.
- (6) Ibid., p. 257.
- (7) Ibid., pp. 260, 261.
- (8) NADC, "The Art of Re-Dyeing," NADC, Silver Spring, Md., 1940, p. 5.
- (9) BEERY, above ed., p. 242.
- (10) Ibid., p. 272.

### CHAPTER IX

# FUR AND GARMENT STORAGE

The havoc wrought on fabrics, especially furs, by various forms of insect life, principally by the larva of the moth, has led the drycleaning industry to devise a means of protection for seasonal garments during the months in which they lie inactive. This protection is known commonly as "storage," or "fur storage," and is usually preceded by some form of cleaning operation.

The functions performed by storage are two: first, any larvae which are already present in the garment are killed; secondly, the garments are protected from the invasion of additional moths or their larva. For the performance of these operations there are two general methods, one involving temperature control, and the other utilizing chemicals, both of which may be used separately or in conjunction.

The first (lethal) process is essentially disinfection. The moths and their larvae may be killed by alternately subjecting them to heat and cold. The garments are placed in the vault and the temperature is brought down to about 50 degrees F. After remaining for several hours at this temperature, the temperature is suddenly lowered to 15 or 18 degrees F. After prolonged exposure to this temperature, the insect life is again subjected to a higher (50 degrees F.) temperature. Repetition of this process for several additional cycles will kill all malignant forms of insect life (1).

This same result may be obtained more easily and more efficiently by the use of a fumigant, or disinfecting gas. A gas, in order to perform satisfactority in this capacity, must possess several definite properties. First, it must be relatively easy to handle, i.e., it must be readily obtainable and the last traces of it must be easily removed from the garment. Second, it must have a maximum toxicity for the insect life and a minimum of toxicity for humans. Lastly, it must not be too expensive. Among the gases which are potential fumigants are sulfur dioxide, chlorine, hydrogen cyanide, and formaldehyde. The first two fumigants mentioned have satisfactory fumigating properties, but also pos-

sess bleaching powers which may damage the fabrics and the dyestuffs. Hydrogen cyanide is quite efficient as a fumigant, but unfortunately has an extremely high toxicity for humans which renders its use unsafe. Formaldehyde, although it is irritating to humans, may be used with comparative safety and is one of the most widely used fumigants for garments. A few other compounds, such as ethyl ether and chloroform, perform satisfactorily, but their costs are prohibitive.

After all insect life has been killed, the garments are placed in the actual storage. The function of this storage is to prevent contamination by more insects. Since it is the larvae, which are formed from the eggs laid in the garments, which do the damage to fabrics, principally to furs, inhibition of hatching of the eggs will prevent further damage. Protection of this type is furnished by keeping the temperature of the storage at about 40 degrees F.; at this temperature and below insect eggs lie dormant and will not hatch (2).

To prevent the laying of eggs after the garment reaches the storage, some sort of a "moth repellant" is used; this principle is employed by housewives in the use of "moth balls." The most important of these agents which keep moths from clothing are naphthalene, camphor (rarely used), ortho- and paradichlorobenzene; of the dichlorobenzenes, the para- form is preferred.

In a storage of this sort, the relative humidity must be kept low to prevent the formation of mildew and mold; conversely, if the relative humidity is too low, drying out of fur pelts will be experienced. Larger installations are equipped with air conditioning and the correct relative humidity is maintained by this means. If the storage is not equipped with air conditioning, it has been found that several shallow receptacles containing anhydrous calcium chloride placed in the corners of the room will prevent excess humidity. The normal opening and closing of the vault under operating conditions usually is a sufficient protection against too little moisture (3).

It is the opinion of drycleaners and other experts in this field that the fumigation process is just as efficient as the so-called "cold-shock" method of disinfection and storage. Nevertheless, the public is convinced that, since fur bearing animals usually live in cold regions, furs are best stored in a refrigerated vault. Because of this fact, many establishments use a combination of both methods; thus they have the advertising value of the "cold" storage plus the economy and convenience of the fumigation method. The trend of installations, however, is toward the vapor or fumigation storage.

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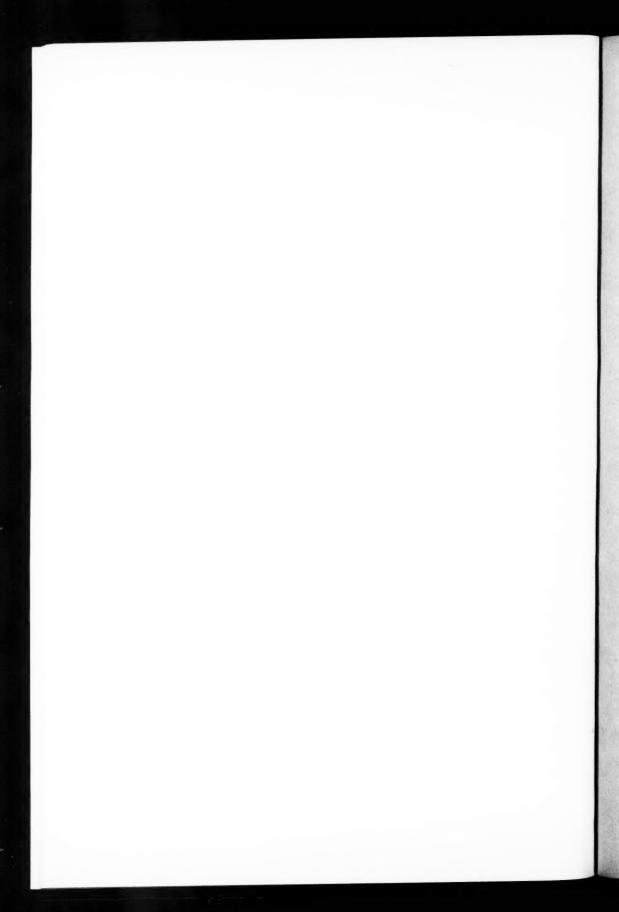
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